



IMPERIAL AGRICULTURAL  
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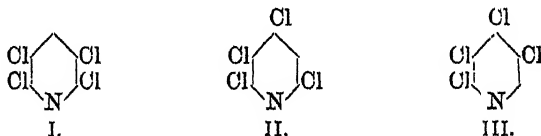
# THE CHEMICAL SOCIETY.

## TRANSACTIONS.

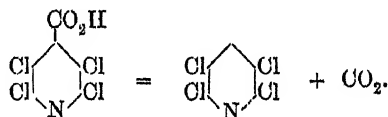
### I.—*The Chlorine Derivatives of Pyridine. Part. IV.* *Constitution of the Tetrachloropyridines.*

By W. J. SELL, M.A., F.I.C., and F. W. DOOTSON, M.A.

IN accordance with the generally accepted view of the constitution of pyridine, there are three theoretically possible derivatives in which four hydrogen atoms may be replaced by the same element or radicle ; and these, in the case of chlorine, may be represented thus :



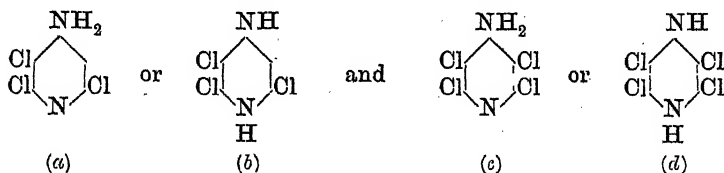
These compounds have all been isolated from the products formed by the action of phosphorus pentachloride on pyridine (*Trans.*, 1898, 72, 432), but in only one case, that of the compound represented by formula I, has the constitution been proved. This substance, which melts at 90—91°, was first obtained by the distillation of tetrachloroisonicotinic acid with glycerol, thus :



Of the two remaining compounds, it was suggested (*loc. cit.*) that the one melting at 21—22° has the chlorine atoms adjacent, that is, the compound is represented by formula III, whilst the compound melting at

74—75° is represented by II. This surmise was founded upon the distinctly greater basic character of the former (m. p. 21—22°), which alone forms a well-defined additive product with mercuric chloride. Direct evidence of the constitution of these compounds was, however, wanting, and it was with the object of supplying this that the present work was undertaken.

In a communication on the synthesis of pyridine derivatives (*Amer. Chem. J.*, 1886, **8**, 377; *Ber.*, 1887, **20**, 2655), Stokes and Pechmann described, among other compounds, two chlorinated derivatives of glutazine to which they gave the alternative formulæ:

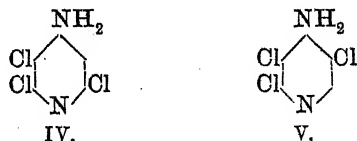


Subsequently (*Trans.*, 1898, **72**, 777), the existence of the amino-group in these compounds was demonstrated, from which it follows that the formulæ (a) and (c) correctly represent the facts.

Now the tetrachloropyridine melting at 21—22° must have the constitution represented by either formula II or III, and if the view already expressed as to its constitution is correct, then it seemed probable, from a consideration of the behaviour of pentachloropyridine and its derivatives towards ammonia, that, on treatment with this agent, the 4- [or  $\gamma$ -] position relatively to the nitrogen would be the one attacked. This was found to be the case, and was shown as follows:

The tetrachloropyridine was treated with ammonia, and the resulting aminotrichloropyridine purified. The latter compound was thereupon further chlorinated by means of phosphorus pentachloride, and an aminotetrachloropyridine obtained identical with (c) above.

It follows therefore, as the only alternatives consistent with the accepted theory, that this aminotrichloropyridine must have one or other of the two formulæ:



A compound represented by formula IV has already been described by Stokes and Pechmann. The new compound, however, differs widely from the description given by them. Although obtained in a state of undoubted purity, it fuses at a lower temperature, gives a

well-defined platinichloride containing  $3\text{H}_2\text{O}$ , forms a beautifully crystalline additive product with mercuric chloride, and can under no conditions be made to yield with bromine water a precipitate which is insoluble in acids (compare *Amer. Chem. J.*, 1886, 6, 377).

In the alternative, therefore, this aminotrichloropyridine must be held to have the constitution represented by the formula V, and as a consequence must have been derived from a tetrachloropyridine of the constitution given by formula III, thus confirming the view previously held.

An attempt to confirm this still further by obtaining the aminotrichloropyridine of formula IV from the tetrachloropyridine melting at  $74-75^\circ$ , which must, of course, have the constitution given by formula II, was unsuccessful. Whilst it was very unlikely that in a compound of this orientation the 4-position would be as reactive as in the other isomerides, it was hoped that the reaction might occur to an extent sufficient to allow of the identification of the compound sought. Want of material prevented further investigation in this direction, as the tetrachloropyridine melting at  $74-75^\circ$  was only isolated in small amount from the product by the action of phosphorus pentachloride or pyridine in sealed tubes, and not at all by the other methods described.

#### EXPERIMENTAL.

Tetrachloropyridine (m. p.  $21-22^\circ$ ) does not appear to be acted on in the cold by aqueous or alcoholic ammonia of any strength. At a temperature of  $130-140^\circ$ , one atom of chlorine is attacked and aminotrichloropyridine,  $\text{C}_5\text{HNC}_3\text{Cl}_3\cdot\text{NH}_2$ , formed. The operation was carried out in sealed tubes and the heating continued for three hours. At the end of that time, practically no unchanged tetrachloropyridine remained in those cases in which an alcoholic solution containing 16 per cent. of ammonia was employed. When aqueous ammonia was used, it was found necessary to continue the heating for a longer time but the same product was obtained. The contents of the tubes were diluted and filtered, and the product purified by crystallisation from dilute alcohol, from which it separates in slender needles. These crystals melted at  $153-153.5^\circ$  (uncorr.), and this melting point was not changed by further recrystallisation. The following numbers were obtained on analysis:

0.1865 gave 0.2075  $\text{CO}_2$  and 0.0265  $\text{H}_2\text{O}$ . C = 30.34; H = 1.58.

0.1950 „ 24.0 c.c. of nitrogen at  $20^\circ$  and 770 mm. N = 14.27.

$\text{C}_5\text{H}_2\text{N}_2\text{Cl}_3$  requires C = 30.44; H = 1.52; N = 14.20 per cent.

The compound is moderately soluble in boiling, and practically

insoluble in cold water, but is freely soluble in the usual organic solvents, and in moderately dilute mineral acids, from which it is precipitated on neutralisation. It sublimes unchanged on heating and is volatile in steam. Its solution in alcohol or hydrochloric acid gives no precipitate with bromine. If a saturated solution of mercuric chloride is added to a solution of the substance in alcohol, an additive compound is formed which crystallises from dilute alcohol in long, silky needles and melts at  $213\text{--}214^\circ$  (uncorr.). A platinichloride is formed on addition of platinic chloride to a solution of the substance in hydrochloric acid or in alcohol. This separates out in thick, golden needles, which are decomposed by boiling water, but can be crystallised apparently unchanged from a dilute solution of platinic chloride in hydrochloric acid. The following numbers were obtained on analysis:

0.3865 lost  $0.0243 \text{ H}_2\text{O}$  at  $100^\circ$  and gave 0.0859 Pt.  $\text{H}_2\text{O} = 6.28$ ;  
Pt = 22.22.

$(\text{C}_5\text{H}_4\text{NCl}_3 \cdot \text{NH}_2)_2 \cdot \text{H}_2\text{PtCl}_6 + 3\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 6.29$ ; Pt = 22.69  
per cent.

*4-Aminotetrachloropyridine*.—This substance was obtained from the preceding compound by the action of an excess of phosphorus pentachloride in sealed tubes at a temperature of  $220\text{--}230^\circ$  maintained for four hours. On cooling, the contents of the tubes were thrown into water, the precipitate collected and crystallised from alcohol, when colourless plates, or, if deposited slowly, cubes, were obtained. These crystals melted at  $214\text{--}215^\circ$  (uncorr.), a temperature somewhat higher than that previously given, and gave the following numbers on analysis:

0.2150 gave 0.5333 AgCl. Cl = 61.33.

0.2605 „ 26.73 c.c. nitrogen at  $20.5^\circ$  and 760 mm. N = 11.71.

$\text{C}_5\text{H}_2\text{N}_2\text{Cl}_4$  requires Cl = 61.14; N = 12.06 per cent.

The properties of this compound agree with those of the aminotetrachloropyridine described by Stokes and Pechmann (*loc. cit.*), and shown by them and by the authors to have the constitutional formula (c) given above. When boiled for two hours with excess of a solution of sodium ethoxide in absolute alcohol, 2-ethoxy-4-aminotrichloropyridine, melting at  $83^\circ$  (uncorr.), was obtained (*Amer. Chem. J.*, 1886, 6, 393), a reaction which affords further confirmation of the identity of the compound.

## II.—*The Dissociation Constants of very Weak Acids.*

By JAMES WALKER and WILLIAM CORMACK.

ALTHOUGH the dissociation constants of many hundreds of organic acids have been measured, chiefly by Ostwald and his pupils, the feeble inorganic acids have been practically neglected in this respect. We are, in consequence, without accurate knowledge of the relative strengths of such common acids as carbonic acid, hydrocyanic acid, sulphydric acid, and boric acid, either relatively to each other or to acetic acid, which may be taken as the typical "weak" organic acid with a definite affinity constant. It is the object of the present communication to supply the necessary data for filling up this blank.

### *The Apparatus and Mode of Experiment.*

As most of the acids investigated were gaseous at the ordinary temperature, a closed form of apparatus had to be devised, which would permit of the solutions being diluted to definite strengths without communication with the air. In a vessel of the usual type, the loss of gas is very rapid, and accurate dilution is impossible.

After several preliminary experiments, the principle finally adopted was that of the syringe. The electrodes were placed at the bottom of a long tube provided with a piston, which, by its regulated withdrawal, could be made to suck into the tube a measured quantity of the water used for dilution. A sketch of the whole apparatus is given in Fig. 1. The principal tube *A* was 46 cm. long and 2.2 cm. in diameter. The stem *P* was made of a glass tube of external diameter only slightly smaller than the bore of *A*, and was closed at the lower end by a rubber stopper *R*, which formed the piston, and fitted closely to the walls of *A*. The external tube was closed at its lower extremity by a perforated rubber stopper provided with slits for the passage of the wires from the electrodes *EE*. These wires were soldered to copper wires *WW*, which made connection with the rest of the apparatus through the mercury cups *MM*. As the tube *A* was immersed in water for at least three-fourths of its length in order that a constant temperature might be secured, great care had to be paid to the insulation of the wires from the electrodes, as the conductivity of the water in the thermostat was much greater than the conductivity of the solutions investigated. The connections are shown on a larger scale in Fig. 2. The copper wires leading to the mercury cups were covered with gutta-percha, and, as an additional precaution, were surrounded by tight-fitting glass tubes throughout the whole length immersed in the water. The connections, together with the lower end of the

tube and the stopper, were embedded in paraffin wax, a short piece of wide rubber tubing being slipped over all before the paraffin wax had set. When the apparatus thus protected was placed in ordinary tap water, no current between the wires could be detected with an induction coil and telephone (compare Ostwald, *Physico-chemical Measurements*, p. 222) if no liquid were inside the apparatus.

The apparatus was filled in the following manner with the solution to be investigated. A bent tube *T* was introduced into one of the holes in the stopper so that connection might afterwards be formed

FIG. 1.

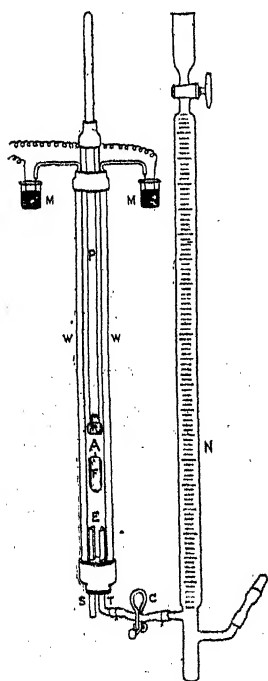
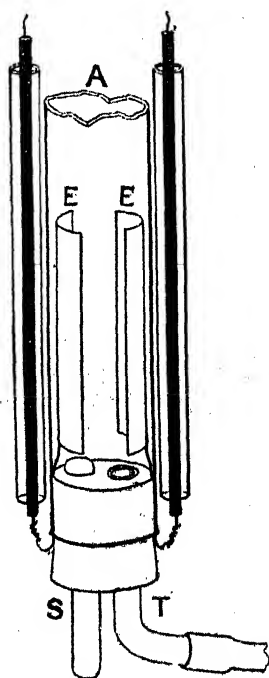


FIG. 2.



with the measuring vessel *N* by means of a short piece of rubber tubing provided with a clip. The syringe was now inverted, and the piston withdrawn, so as to leave a little more than 20 c.c. clear space above it. By means of a pipette or burette, 20 c.c. of the liquid to be examined were delivered into the apparatus through the other hole in the stopper, which was then closed by a glass plug, the piston being thereafter forced upwards until the liquid reached the end of the tube *T*. The measuring tube *N*, which, together with the connection tube, had been previously completely filled with water, was now attached to



*T*, communication between the two vessels being prevented by the pinch-cock *C*. Both the rubber tube and bent glass tube were chosen of narrow bore so as to prevent mixing of the liquids when the pinch-cock was open. The whole apparatus was now placed in the upright position in a thermostat containing water at 18°, at which temperature all measurements in this paper were made. The thermostat consisted of a tall enamelled cylinder of about 20 litres capacity, the outer vessel of a steam steriliser being found very suitable. The mercury cups *MM* were fixed in a copper stage fastened to the rim of the thermostat.

The measurements were made with induction currents and telephone in the manner described by Kohlrausch and Holborn (*Leitvermögen der Elektrolyte*). For the weakest acids measured, the electrodes were not platinised; for stronger acids, like carbonic acid, they were platinised with Lummer and Kurlbaum's solution. In order to wash the electrodes free from conducting substances after platinisation, we first of all electrolysed a solution of sodium acetate between them as recommended by Walker and Hambly (*Trans.*, 1897, 71, 63), after which no difficulty was experienced in rendering them fit for use in a few hours by treatment with water. All the rubber parts of the apparatus were subjected to the prolonged action of water before being used, and did not affect the conductivity of the purest water we employed during the time necessary for completing a series of dilutions.

After the first measurement of the conductivity had been made, the solution was diluted by the addition of 20 c.c. of water, which was admitted by opening the clip *C* and the stopcock of the measuring tube (a Schiff nitrometer), the piston being then carefully withdrawn until the level of the water in the measuring tube reached the 20 c.c. mark. The clip and stop-cock were then closed, and the diluted solution thoroughly mixed by inverting the conductivity vessel several times. The mixing was effected by the glass float *F* of approximately the same specific gravity as water. The apparatus was then replaced in the thermostat, and a reading of the conductivity made when temperature equilibrium had been established. The solution was again mixed and another reading taken. If this differed from the first, the operations were repeated until a constant value was obtained, which occurred, as a rule, in less than fifteen minutes. The dilution was now continued by the addition of another 20 c.c. of water in the manner previously described, the level of the water in the nitrometer now standing at the 40 c.c. mark. In this way, four to five dilutions by successive increments of 20 c.c. could be made in little more than an hour, without the solution coming in contact with the air during the process.

*Preparation of the Water used for Dilution.*

We found no difficulty in obtaining a supply of water with a conductivity of  $0.7 \times 10^{-6}$  in Siemens units, at  $18^\circ$ , by three successive distillations, namely, with alkali, with phosphoric acid, and, finally, without the addition of any chemical. The last distillation is the most important, and must be conducted in a room containing no volatile acids or alkalis, the atmosphere even of a well ventilated chemical laboratory being fatal to the preparation of water of the above quality. In this last distillation, the water was condensed in a tin pipe, the end of which passed through the rubber stopper of a bottle which was further provided with a glass syphon tube and a long, narrow inlet tube for air. In this bottle, the water suffered no deterioration in quality even when kept for several days. It is essential, if weak acids are to be investigated, that the conductivity of the water used for the preparation and dilution of the solutions should not exceed the above value, otherwise errors of unknown magnitude are introduced into the determinations of the conductivity. The conducting power of water of the conductivity  $0.65 \times 10^{-6}$  is due to dissolved carbonic acid almost entirely, and it will be shown in the sequel that the error thereby introduced into the conductivity of other weak acids is not only very small, but can be estimated and eliminated with moderate accuracy.

*Carbonic Acid.*

When carbon dioxide dissolves in water, the solution produced possesses a considerable electrical conductivity, indicating the formation of the acid  $\text{H}_2\text{CO}_3$ . The conductivity of such solutions have already been measured by Pfeiffer (*Ann. Phys. Chem.*, 1884, 23, 625) and by Knox (*ibid.*, 1895, 54, 44). The solutions studied by Pfeiffer were prepared under pressure, and are therefore somewhat too concentrated to be of service in fixing the dissociation constant of carbonic acid; the solutions investigated by Knox, on the other hand, are sufficiently dilute to permit of a constant being calculated, although Knox did not seek to perform the calculation himself.

Knox's results are given in the following table, the letters bearing their usual signification, namely:

$v$  = Dilution, or number of litres in which 1 gram-molecule is contained.

$\mu$  = Molecular conductivity.

$m$  = Proportion of acid dissociated.

$k$  = Dissociation constant, or the value of the expression  $\frac{m^2}{(1-m)v}$ .

In calculating the dissociated proportion, the molecular conductivity of carbonic acid at infinite dilution was made equal to 336 at 18°, the data used in fixing this number being given below.

<i>v.</i>	$\mu$ .*	<i>m.</i>	<i>k.</i>
12.61	0.731	0.00217	0.00376
14.54	0.789	0.00235	379
18.43	0.877	0.00261	370
24.9	1.025	0.00305	375
36.36	1.233	0.00367	372
53.2	1.487	0.00443	370
74.3	1.756	0.00523	370
125	2.300	0.00684	377
287	3.520	0.01048	386
1099	7.540	0.02244	469

The constancy of the expression *k* for a tenfold increase in the dilution leaves nothing to be desired. At the two greatest dilutions, the constant increases rapidly owing to the conductivity of the water used in preparing the solutions, for which no correction has been made in the calculation.

Before beginning our own experiments on the conductivity of carbonic acid, we made a series of measurements on the conductivity of solutions of sodium hydrogen carbonate, in order to obtain the data necessary for the calculation of the conductivity of carbonic acid at infinite dilution. As it was possible that the sodium hydrogen salt might undergo some degree of hydrolysis at the greatest dilutions we investigated, two series of experiments were made. In one set, the solution was diluted with water in the usual manner by means of pipettes. In the other set, the diluent employed was a solution of carbonic acid, in order that the extent of hydrolysis might be reduced (compare Bredig, *Zeit. physikal. Chem.*, 1894, 13, 214). Both sets yielded practically the same result, as indeed might have been expected, the magnitude of the dissociation constant of carbonic acid indicating that the extent of hydrolysis of sodium hydrogen carbonate would not exceed a fraction of a per cent. even at the greatest dilution we investigated. The molecular conductivities here, as throughout this paper, are expressed in Siemens units, a 0.02-normal solution of potassium chloride with molecular conductivity equal to 112.2 at 18° having been taken as the standard of reference.

\* The molecular conductivities in the abstract of Knox's paper (*Zeit. physikal. Chem.*, 1895, 17, 186) have been reduced to half the true value by an inadvertence in the recalculation; the dissociation constant given there is consequently erroneous.

*Sodium hydrogen carbonate, Na·HCO<sub>3</sub>'.*

v.	μ.
32	65·6
64	68·6
128	71·1
256	73·9
512	76·0

These numbers point to a conductivity of 79·5 for sodium hydrogen carbonate at infinite dilution (compare Bredig, *loc. cit.*, 198). Subtracting from this total value the number 41·5 for sodium (Kohlrausch), we are left with the value 38 for the ion HCO<sub>3</sub>'. To this we must now add the value 298 for the hydrogen ion (Kohlrausch), and thereby obtain the number 336 as the molecular conductivity of carbonic acid, H·HCO<sub>3</sub>' at infinite dilution.

The carbonic acid used by us was prepared from marble and hydrochloric acid, and was washed by passing through two wash-bottles and finally a Geissler potash bulb all filled with pure water. The gas was then bubbled through water of minimum conductivity contained in a carefully cleansed bottle. To estimate the concentration of the solution thus obtained, we employed Pettenkofer's method, the titrations being made with fortieth-normal solutions of baryta and hydrochloric acid.

The following table gives the conductivity results for carbonic acid solutions prepared in this way :

*Carbonic acid, H<sub>2</sub>CO<sub>3</sub>, from marble.*

v.	μ.	m.	k.
31·25	1·038	0·00309	0·0 <sub>0</sub> 306
62·5	1·475	0·00439	309
93·7	1·800	0·00536	308
125	2·083	0·00620	309

Mean.....0·0<sub>0</sub>308

As a very slight amount of impurity, say hydrochloric acid, would considerably affect the conductivity of a weak acid such as carbonic acid, another solution was prepared by passing the gas generated by the slow evaporation of solid carbon dioxide, first through pure water to wash it, and then through water of minimum conductivity. In this way, it was thought that the presence of all conducting impurities would be avoided. As the subjoined table indicates, practically the same numbers were obtained as for carbonic acid from marble

*Carbonic acid,  $\text{H}_2\text{CO}_3$ , from solid carbon dioxide.*

<i>v.</i>	<i>μ.</i>	<i>m.</i>	<i>k.</i>
27.5	0.972	0.00289	0.0 <sub>6</sub> 305
55.0	1.368	0.00407	303
82.5	1.679	0.00500	304
110.0	1.930	0.00575	302

Mean.....0.0<sub>6</sub>304

The value of the constant calculated from our experiments is thus about 20 per cent. less than the value calculated from Knox's numbers, corresponding to an actual difference in the conductivity of 10 per cent. In view of the small conductivity of the solutions investigated, this difference cannot be said to be excessive, and is probably to be accounted for as follows. In the first place, the water which we used for the dilutions was of distinctly better quality than that employed by Knox, the conductivity of which varied from  $0.95 \times 10^{-6}$  to  $2.6 \times 10^{-6}$ , and was especially large for the most dilute solutions where its proportionate influence is greatest. Thus at the dilution 125, the conductivity of the water amounted to 12 per cent. of the total conductivity of the solution. It is clear, therefore, that this alone might go a long way in accounting for the larger numbers obtained by Knox. The mode of measuring the concentration of the solutions was also different in the two cases. Whilst we used a chemical method for estimating the carbonic acid in the solutions examined by us, Knox determined the amount dissolved by measuring the pressure of carbon dioxide with which the solution was in contact, and then calculating from Bunsen's absorption coefficient for  $18^\circ$  by means of Henry's law. Now Bunsen's number may be affected by an error of several per cent., as a reference to his paper (*Liebig's Annalen*, 1855, 93, 1) will show, and it is by no means certain that Henry's law is accurately true throughout the range of pressures considered. We are therefore disposed to adhere to our own numbers as being probably the more accurate, notwithstanding the satisfactory constancy of the expression *k* exhibited when Knox's values are used in the calculation.

*Conductivity of Water Distilled in Air.*

On the assumption that Henry's law was valid, and that the conductivity varied inversely as the square root of the dilution, which is very nearly the case for carbonic acid, Knox calculated what the conductivity would be if the water was saturated with carbon dioxide at a pressure equal to the partial pressure of the gas in atmospheric air. The result given in his paper, viz.,  $0.56 \times 10^{-6}$  in reciprocal Siemens units,

is, however, erroneous, owing to an arithmetical error in the last equation (*loc. cit.* p. 57). The correct number deduced from his data is  $0.725 \times 10^{-6}$ .

A more accurate value can be calculated from the dilution formula,

$$k = \frac{m^2}{(1-m)v},$$

as follows. At  $18^\circ$ , the dilution of a solution saturated with carbon dioxide at a pressure of 760 mm. is, according to Bunsen's absorption data, equal to 24 litres. If the partial pressure of carbon dioxide in air is 0.0003 atmosphere, the dilution of a solution saturated at this pressure will be  $24/0.0003 = 80000$ . If, then, in the above equation we substitute 0.000000304 for  $k$  and 80000 for  $v$ , we obtain  $m = 0.144$ , that is, 14.4 per cent. of the carbonic acid dissolved from normal air by pure water is dissociated into the ions  $H^+$  and  $HCO'_3$ . From the degree of dissociation  $m$  we obtain the molecular conductivity  $\mu$  by multiplication with 336, the maximum molecular conductivity of carbonic acid at  $18^\circ$ . From this value, namely, 48.4, we obtain the specific conductivity on dividing by the dilution in cubic centimetres, so that we have the conductivity  $48.4/80,000,000 = 0.605 \times 10^{-6}$  for water which has been in contact with the atmosphere at  $18^\circ$ .

It is highly improbable that Henry's law in an unmodified form can be applied with propriety to such a case as that discussed above. From the study of analogous cases, it appears much more likely that the concentration of the gas in the air bears a constant ratio to that of the *undissociated portion* of the dissolved gas, rather than to the concentration of the *total* dissolved gas. The dilution of the undissociated portion  $1-m$  thus becomes 80000, and the dilution of the whole gas dissolved 69000. Calculating in the same manner as above described, we obtain the value  $0.65 \times 10^{-6}$  for the conductivity of water which has been in contact with air. If we use the constant derived from Knox's numbers, the values become  $0.67 \times 10^{-6}$  and  $0.71 \times 10^{-6}$  for the unmodified and modified forms of application of Henry's law respectively.

Kohlrausch (*Zeit. physikal. Chem.*, 1894, 14, 321) found that water prepared in a vacuum and of conductivity  $0.11 \times 10^{-6}$ , gained in conductivity on being left in contact with the air until the value  $0.60 \times 10^{-6}$  was reached. It is also stated by Kohlrausch and Holborn (*loc. cit.*, p. 111) that the lowest conductivity obtainable for water distilled in air is  $0.65 \times 10^{-6}$ . It will be seen that these values are in excellent agreement with those calculated from our experiments, so that we may assume with confidence that carbon dioxide is the only substance in the atmosphere which confers conductivity on water.

*State of Carbon Dioxide in Aqueous Solution.*

In what has been said above, it is assumed that all the dissolved carbon dioxide exists in the aqueous solution as carbonic acid,  $\text{H}_2\text{CO}_3$ . This is by no means necessarily the case, for a large proportion might exist in the solution as carbon dioxide without entailing any alteration in the apparent dissociation constant. We may suppose, for example, that only half of the dissolved carbon dioxide exists in the solution as  $\text{H}_2\text{CO}_3$  and its dissociation products  $\text{H}^+$  and  $\text{HCO}_3^-$ . If  $v$ , as before, represents the volume in which 1 gram-molecule of the carbon dioxide is dissolved, irrespective of the condition it assumes in the dissolved state, the dilution formula becomes

$$(\frac{1}{2} - m)v$$

since the quantity of  $\text{H}_2\text{CO}_3$ , which was formerly 1, is now only  $\frac{1}{2}$ . Now, in solutions of this strength which we investigated,  $m$  does not amount to more than 0.006, so that we can write the dilution formula in the form

without sensible error. If only half of the dissolved gas is contained in the solution as  $\text{H}_2\text{CO}_3$ , this formula becomes

$$m$$

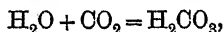
We have therefore  $k' = 2k$ . The real dissociation constant of the acid  $\text{H}_2\text{CO}_3$  would therefore, in this case, be twice the apparent dissociation constant, namely, equal to 0.00608. In general, if  $1/n$  represents the fraction of the total dissolved carbon dioxide which exists in the solution as  $\text{H}_2\text{CO}_3$ , the dissociation constant for the acid will be  $nk$ , where  $k$  is the apparent dissociation constant calculated from our experiments. What is here stated holds good, however, only for moderate degrees of dilution and for moderate values of  $n$ , for as soon as  $m$  becomes of dimensions approaching those of  $1/n$ , the simple formula can no longer be applied.

We have assumed above that the proportion of the dissolved gas which remains as  $\text{CO}_2$  is constant and independent of the dilution of the solution. This assumption is justifiable, since the active mass of the solvent water must remain sensibly constant for dilute solutions, and the quantity converted into  $\text{H}_2\text{CO}_3$  will therefore be proportional to the quantity dissolved. It is possible, however, that the equilibrium is between the  $\text{CO}_2$  in solution and the *undissociated*  $\text{H}_2\text{CO}_3$ , not

the whole amount of  $\text{H}_2\text{CO}_3$  and its dissociation products. For moderate dilutions and moderate values of  $n$ , this latter assumption in no way alters the deductions given above.

Since we obtain a constant value of  $k$  for dilutions up to 125 litres, the value of  $n$  cannot be very great—cannot, for instance, well be more than 5, for otherwise Ostwald's dissociation formula would not be applicable in its simple form. The agreement, too, between the actual and calculated values of the conductivity of water which has absorbed carbon dioxide from normal air points to the value of  $n$  being small, probably not greater than 2. We may take it, then, as fairly certain that when carbon dioxide dissolves in water, at least half of the dissolved substance exists in the form of the acid  $\text{H}_2\text{CO}_3$ .

It is only the apparent dissociation constant which is of interest to us, however, for it is that which enables us to calculate the strength of carbonic acid in solution as an accelerator, as a conductor of electricity, or as competing for a base against other acids. A knowledge of the real constant, and of the constant regulating the equilibrium,



would be of undoubted theoretical interest, but for practical purposes and ordinary solutions, the apparent constant supplies us with all the information necessary for the treatment of problems likely to occur.

### *Hydrogen Sulphide.*

In 1885, Ostwald determined the conductivity of hydrogen sulphide, and found that it was very small. No constant can be calculated from his numbers, however, as at that date the influence of the quality of the water employed in making the solutions was insufficiently understood. We therefore made several determinations with the best water we could obtain, and with hydrogen sulphide as free as possible from foreign conducting matter.

The hydrogen sulphide was prepared by the action of hydrochloric acid on a very concentrated solution of pure sodium sulphide, and was subjected to no other purification than thorough washing with water, the final washing taking place through water contained in a Geissler potash apparatus. If the hydrochloric acid is added at such a rate that the disengagement of hydrogen sulphide is slow and steady, the method gives a product of constant conductivity. The strengths of the solutions thus prepared were estimated by adding a measured quantity of the solution to a known excess of silver nitrate solution, filtering, and determining the amount of silver in the filtrate by Volhard's method.

The maximum conductivity of hydrogen sulphide, treated as the



monobasic acid  $\text{H}\cdot\text{HS}'$ , was fixed by means of measurements of the conductivity of sodium hydrosulphide,  $\text{NaHS}$  (Walker, *Proc. Roy. Soc. Edin.*, 1893-4, 255). These measurements give 58 as the ionic rate for  $\text{HS}'$ , and therefore 356 as the maximum conductivity for hydrogen sulphide at  $18^\circ$ .

*Hydrogen sulphide,  $\text{H}\cdot\text{HS}'$ .*

<i>v.</i>	$\mu$ .	<i>m.</i>	<i>k.</i>
25	0.426	0.00119	0.0,572
50	0.599	0.00168	568
75	0.731	0.00205	562
100	0.854	0.00240	577
125	0.944	0.00265	568

Mean..... 0.0,569

Another similar set of experiments at somewhat smaller dilutions gave the mean value 0.0,574, which is practically identical with the former result.

Since the impurity in the water used for dilution is carbonic acid, the dissociation constant of which is known, it is possible to correct the individual values of the conductivity by using the dissociation equations for the separate acids. As the correction in this case, however, is of very small dimensions, it may be neglected without sensible error. An example of the method of calculation employed in the correction will be given when the conductivity of phenol is under consideration.

*Hydrocyanic Acid.*

We are again indebted to Ostwald for measurements of the electric conductivity of hydrocyanic acid. He found the conductivity to be considerably smaller than that of hydrogen sulphide, but, as before, his numbers are not sufficiently accurate to permit of the calculation of a dissociation constant, owing to the uncertain correction for the conductivity of the water employed as solvent.

In our experiments we used water of conductivity not exceeding  $0.65 \times 10^{-6}$ , and even with water of this quality experienced much difficulty in obtaining satisfactory solutions. The method we finally adopted for preparing solutions of hydrocyanic acid was first to prepare a liquid acid very nearly free from water, and then allow the vapour of this to pass slowly into the water of minimum conductivity. The liquid hydrocyanic acid was obtained by gently heating a mixture of potassium ferrocyanide and glacial phosphoric acid with an equal bulk of water, and condensing the vapour in a cooled distilling flask. When a sufficient quantity had been collected, the

distilling flask was disconnected from the generating apparatus and attached to a delivery tube which dipped beneath the surface of the water used as solvent. As the conductivity of the hydrocyanic acid was very small, the solutions were made as strong as was consistent with the theoretical possibility of obtaining a constant value for the expression  $k$ . It was found that non-platinised electrodes gave better results than those which had been platinised.

Kohlrausch has shown that the molecular conductivity of potassium cyanide in concentrated solutions (normal and semi-normal) is intermediate between the molecular conductivities of equivalent solutions of potassium chloride and potassium iodide. As these two salts have practically the same molecular conductivity for infinite dilution, it was assumed that the conductivity of potassium cyanide would have a maximum value equal to 121.6, which gives 60 for the ion  $\text{CN}'$  and 358 for the conductivity of  $\text{HCN}$  at infinite dilution.

The concentration of the original solution was determined with silver nitrate solution according to Liebig's method.

*Hydrocyanic acid,  $\text{H}\cdot\text{CN}'$ .*

$v$	$\mu$	$m$	$k$
2	0.0183	0.0000512	0.0 <sub>8</sub> 131
4	0.0262	738	133
8	0.0320	894	133
16	0.0365	1019	130

Mean..... 0.0<sub>8</sub>132

Another set of experiments gave a mean value of 0.0<sub>8</sub>14, and several preliminary experiments gave still higher values. We have chosen the smallest value as being the most probable, owing to the fact that any possible impurity would increase the conductivity and thus the constant.

The constant as it stands is probably still too high, for even the presence of the carbonic acid in air-saturated water would effect an increase of about 2 per cent. on the mean value.

*Boric Acid.*

Kahlenberg and Schreiner (*Zeit. physikal. Chem.*, 1896, 20, 547) have shown that in all probability only one boric acid exists in solution, namely,  $\text{H}_3\text{BO}_3$ , and that in dilute solutions the only stable salt is of the type  $\text{NaH}_2\text{BO}_3$ . From their conductivity numbers, it would appear that the maximum conductivity of the salt  $\text{NaH}_2\text{BO}_3$  is about 75.0 at 18°. Now this number is certainly too great, as Shields has proved

that a decinormal solution of borax is hydrolysed to the extent of one-half per cent. The conductivity of the sodium hydroxide produced by the hydrolysis is much greater than that of an equivalent solution of the boric acid salt, so that we must make a deduction of at least 3 per cent. in order to obtain an approximate value of the maximum conductivity of the non-hydrolysed salt; this would lead to a value of somewhat more than 72. In order to check this result, we made a series of determinations of the conductivity of the salt at  $18^{\circ}$ , using a 0.025-normal solution of boric acid as dilution liquid in order to diminish the hydrolysis. From our experiments, we deduced the value 71.5 as the maximum conductivity of the salt  $\text{NaH}_2\text{BO}_3$ , supposing hydrolysis to be absent. This value would give 328 as the maximum conductivity of the acid  $\text{H}_3\text{BO}_3$  if the dissociation is into the ions  $\text{H}^+$  and  $\text{H}_2\text{BO}_3^-$ .

The boric acid we employed in our experiments was thrice recrystallised from pure water in a platinum vessel, and the solution made up by weight. The electrodes used in the final experiments were not platinised, but platinisation did not seem to affect the accuracy of the method or alter the numbers obtained.

*Boric acid,  $\text{H}\cdot\text{H}_2\text{BO}_3^-$ .*

<i>v.</i>	<i><math>\mu</math>.</i>	<i>m.</i>	<i>k.</i>
11.1	0.0450	0.0000137	0.0 <sub>8</sub> 170
22.2	0.0636	194	169
33.3	0.0783	239	171
44.4	0.0891	272	166

Mean..... 0.0<sub>8</sub>169

Another set of experiments yielded the mean value 0.0<sub>8</sub>170.

This constant is of the same magnitude as that for hydrocyanic acid, and a similar correction would have to be applied to eliminate the effect of the conductivity of the carbonic acid in the water employed for dilution.

Bock (*Ann. Phys. Chem.*, 1887, 30, 638) made some observations on the electric conductivity of boric acid solutions at  $18^{\circ}$ , but the solutions he employed were stronger than ours, and the results he obtained do not yield a value for *k* which is even approximately constant. If, however, we take his most dilute solution, which is comparable with our strongest solution, we obtain the following:

<i>v.</i>	<i><math>\mu</math>.</i>	<i>m.</i>	<i>k.</i>
8	0.0386	0.0000118	0.0 <sub>8</sub> 174

This value is in excellent accordance with that obtained in our own experiments.

*Phenol.*

Bader (*Zeit. physikal. Chem.*, 1890, 6, 289) has given numerous data for the conductivity of the phenols and their substitution products. Many of the substitution products yield definite dissociation constants, but this is not generally the case with the simple phenols themselves. Thus he obtains for phenol,  $C_6H_5\cdot OH$ , the following values at  $25^\circ$ :

$v.$	$\mu.$	$k.$
25	0.14	0.0056
50	0.23	0.77
100	0.41	120

Here the value of the expression  $k$  varies greatly, a fact which is possibly due to the character of the water employed in the dilutions. Bader gives no figures from which we can judge the quality of this water.

As we suspected that Bader's numbers for phenol were considerably too high, we determined the conductivity of as pure a solution as we could produce. A quantity of colourless crystallised phenol was shaken up in a stoppered cylinder with successive small quantities of pure distilled water in order to remove any conducting substance which the phenol might contain. A solution of this purified phenol was then made up by weight, the phenol being assumed to have taken up 26 per cent. of water, in accordance with the experiments of Alexéeff. The results we obtained were as follows:

$v.$	$\mu.$	$m.$
10	0.0132	0.000041

It will be seen that this value is only about one-tenth of that obtained by Bader for the molecular conductivity under corresponding conditions of temperature and dilution. But this value must itself be too great. The specific conductivity of the water used to prepare the solution was  $0.65 \times 10^{-6}$ , the specific conductivity of the solution being only twice this magnitude, namely,  $1.32 \times 10^{-6}$ . We are not justified in assuming, however, that the conductivity of the phenol is equal to the difference of these two numbers, for if carbonic acid is the impurity present in the water, each acid will lower the dissociation, and therefore the conductivity, of the other, so that the correction will not be so large as at first sight appears. The mode of correction is as follows.

For the maximum conductivity of phenol, we have the number 322 according to the rule established by Ostwald for organic acids. The degree of dissociation of the phenol solution is therefore 0.000041 if we take the uncorrected conductivity. The concentration of the

hydrogen ions is therefore one-tenth of this, namely,  $41 \times 10^{-7}$ , and this number is practically correct, since the hydrogen ions are responsible for at least seven-eighths of the conductivity, and the difference in the speeds of the carbonate and phenolate ions vanishes in comparison. The equilibrium in the case of carbonic acid is regulated by the equation

$$\frac{(\text{H ions}) \times (\text{HCO}_3 \text{ ions})}{(\text{H}_2\text{CO}_3)} = 3.04 \times 10^{-7},$$

the quantities in brackets indicating concentrations in gram-molecules per litre. Now the total concentration of the carbonic acid dissolved from the air is  $125 \times 10^{-7}$  in the same units. If  $n$  is taken to represent the concentration of the  $\text{HCO}_3$  ions, we have thus the equation

$$\frac{41 \times 10^{-7} \times n}{(125 \times 10^{-7}) - n} = 3.04 \times 10^{-7},$$

whence  $n = 9 \times 10^{-7}$ . The number of hydrogen ions coming from the carbonic acid in the water is therefore  $9 \times 10^{-7}$ . This deducted from the total concentration of hydrogen ions leaves  $32 \times 10^{-7}$  as the concentration of hydrogen ions derived from the phenol, so that this number also represents the concentration of the  $\text{C}_6\text{H}_5\text{O}$  ions. Now the product of the hydrogen and phenolate ions in the above solution must be equal to the product of the same magnitudes for a solution of phenol in water free from carbonic acid. If  $d$  therefore represents the concentration of dissociated phenol in the pure solution, we have

$$\begin{aligned} d^2 &= 41 \times 10^{-7} \times 32 \times 10^{-7} \\ d &= 36 \times 10^{-7}, \end{aligned}$$

whence we obtain as the degree of dissociation of a pure decinormal solution of phenol,  $n = 0.000036$  instead of the uncorrected value, 0.000041.

Using this corrected value, we find  $k = 0.0_{13}$  as an approximate value of the dissociation constant of phenol, that is, about one-fortieth of Bader's smallest value of  $k$ .

#### *Acetylene.*

Jones and Allen (*Amer. Chem. J.*, 1896, 18, 1) give numbers for the conductivity of acetylene which are very much too high, probably as the result of some arithmetical error. The values they obtained when recalculated from equivalent into molecular weights indicate that acetylene is a stronger acid than acetic acid, which is certainly not the case.

We made a single experiment in order to determine the magnitude of the conductivity of aqueous solutions of acetylene. The acetylene

was prepared from calcium carbide and purified by washing in successive bottles containing silver nitrate solution, the gas being thereafter thoroughly washed with pure water. A small quantity of pure water was then saturated with the gas at the atmospheric pressure. Since water dissolves about its own volume of acetylene at the ordinary temperature, the dilution of the solution thus obtained would be approximately 23, a number which we confirmed by precipitating with ammoniacal silver nitrate, filtering, and titrating the excess of silver in the filtrate with ammonium thiocyanate. The conductivity of this solution was only one-fourth greater than that of the solvent water, and this slight rise might conceivably be due in great part to the presence of a trace of some conducting impurity. We must therefore conclude that acetylene has very feeble acid properties, its dissociation constant being less, and in all probability much less, than that of phenol.

*Summary.*

The following table contains the dissociation constants of the acids which we investigated, the constant of acetic acid being added for comparison :

Acid.	$k \times 10^{10}$ .
Acetic .....	180000
Carbonic .....	3040
Hydrogen sulphide .....	570
Boric .....	17
Hydrocyanic .....	13
Phenol .....	1.3

A better idea of the relative strengths of the acids, however, may be formed from the subjoined table, which shows the percentage dissociation of the acids in decinormal solution. The numbers for hydrochloric and acetic acids are derived from the data given by Kohlrausch and Holborn (*loc. cit.*), the numbers for the other acids being calculated from the dissociation constants found by ourselves.

*Percentage degree of dissociation in decinormal solution.*

Acid.	100 m.
Hydrochloric .....	91.4
Acetic .....	1.30
Carbonic .....	0.174
Hydrogen sulphide .....	0.075
Boric .....	0.013
Hydrocyanic .....	0.011
Phenol .....	0.0037

These numbers, inasmuch as they are proportional to the avidities, give a practical indication of the strengths of the acids. Thus, if acetic and carbonic acid compete for a monacid base, all three substances being in molecular decinormal solution, the base will be shared between the acids in the ratio 1·3 : 0·174, that is, the acetic acid will take eight parts of the base for one taken by the carbonic acid. Again, if carbonic acid and hydrogen sulphide compete in equivalent quantities for an equivalent of a base, the carbonic acid will take seven-tenths, and the hydrogen sulphide three-tenths. In the extreme case of hydrochloric acid competing against phenol in decinormal solution, the phenol gets only 1 part in 22000.

For acids weaker than acetic acid, the degrees of dissociation are in the ratios expressed by the above table for practically all dilutions, since they are, in fact, proportional to the square roots of the dissociation constants. All the acids in the table have been treated as monobasic acids, so that molecular quantities are always considered, not equivalent quantities. We are justified in proceeding thus, for each acid in competing with another acid for an insufficient quantity of a base, behaves in the first instance as a monobasic acid. Possibly the assumption would not be quite accurate for the case of carbonic acid competing for an equivalent of base against phenol, but where the polybasic acid is the weaker of the competing pair, the assumption is in every case justifiable.

As to the probable accuracy of the numbers, it may be said that the conductivities and constants for the weakest acids are undoubtedly somewhat too high. We are of opinion, however, that the error is in no case very considerable, for our results are in close agreement with the hydrolysis determinations of Shields (*Phil. Mag.*, 1893, [v], 35, 365), data now being available for the comparison of the two methods. A discussion of this connection between the conductivities of the weak acids and the extent of hydrolysis of their salts in aqueous solution will appear in another place.

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### III.—*The Preparation and Properties of Solid Ammonium Cyanate.*

By JAMES WALKER and JOHN K. WOOD.

WHEN a solution of ammonium cyanate (prepared by the double decomposition of silver cyanate and ammonium chloride) is evaporated to dryness, either on a water-bath or in a vacuum at the ordinary

temperature, the residue is found to consist entirely of urea, the transformation of the cyanate into urea taking place at an ever-increasing rate as the concentration of the solution becomes greater (Walker and Hambly, *Trans.*, 1895, 67, 746). In alcoholic and other solutions, the conversion of ammonium cyanate into urea is still more rapid (Walker and Kay, *Trans.*, 1897, 71, 489), so that, in order to obtain pure ammonium cyanate, it is necessary to prepare it directly in the solid state.

Liebig and Wöhler (*Ann. Phys. Chem.*, 1830, 20, 393) attempted to prepare it by direct union of ammonia and cyanic acid, both substances being in the form of gases. They describe their experiments as follows: "When the vapour of the acid was passed into dry ammonia gas contained in a wide glass tube over mercury, the tube became warm and the gases condensed to a cloud which soon settled on the inner wall of the vessel as a microcrystalline, very voluminous, woolly mass. In order to obtain it in larger quantity and free from the impurity of mercury, we brought the gases into contact in a dry flask. The cloud which was formed with simultaneous heating of the flask was deposited as a loose, snow-white powder, and at the mouth of the tube which delivered the cyanic acid gas there was produced a thick woolly vegetation, which, on account of the heat evolved, soon melted to clear drops which fell from the tube." They showed that the loose powder gave the reactions of a cyanate, the clear drops being urea produced from the cyanate by the heat of the reaction. The powder, when left over mercury in presence of ammonia, remained unchanged for a week. Left in a vessel loosely covered with paper, it continuously gave off ammonia, and in two days was almost entirely converted into urea. Both the freshly prepared cyanate and the urea formed by its transformation left a residue of much "insoluble cyanuric acid" (cyamelide) when treated with water. "From these facts it appears then that ammonium cyanate is a basic salt, which undergoes transformation into urea with loss of ammonia."

It seemed to us likely that if we could prevent the heat produced by the union of the ammonia and the cyanic acid vapour from raising the temperature to a point at which ammonium cyanate was decomposed or transformed, we might be able to obtain the normal cyanate in the pure state, and free from any admixture of urea or cyamelide. The method we at first adopted was to mix ethereal solutions of the reacting substances at the temperature of a good freezing mixture, and this we found to be successful.

A wide glass tube was bent at an obtuse angle, and the horizontal portion charged with anhydrous cyanuric acid. The other limb passed downwards through a cork closing the mouth of a wide test-tube, and dipped beneath the surface of anhydrous ether which the



test-tube contained. This ether was kept at a temperature not exceeding  $-17^{\circ}$  by means of a freezing mixture. The cyanuric acid in the horizontal limb was gradually heated with a Ramsay burner, a moderately rapid stream of hydrogen being at the same time passed through the tube in order to carry over the resulting cyanic acid vapour into the ether, in which the bulk of it dissolved. It is impossible to avoid the condensation of a considerable portion of the cyanic acid vapour to form cyanuric acid or cyamelide, so that, unless the tube chosen is at least half an inch in diameter, it is apt to become blocked before the experiment is completed. We now freed the ethereal solution of cyanic acid from cyamelide and other solid matters by filtration through a dry filter, and mixed it with a solution of ammonia in anhydrous ether in such proportions that the acid remained in slight excess. As a rule, the ethereal solution of ammonia was also cooled to the temperature of the freezing mixture, but experiments showed that this was not absolutely necessary. A flocculent, semi-gelatinous precipitate separated as soon as the solutions were mixed, and the temperature did not rise more than a few degrees, the heat of the reaction being mostly absorbed in warming the solvent. The precipitate was collected as rapidly as possible with the aid of a filter-pump, and freed from ether in an exhausted desiccator over sulphuric acid. In the case of some samples used for analysis, moisture was carefully excluded during the process of filtration, and the temperature was kept below zero by means of a freezing mixture surrounding the filter-tube.

When the ether had been entirely removed from the precipitate, the latter presented the appearance of a pure white mass, caked together and very friable. It dissolved completely in water, the solution having a perfectly neutral reaction to litmus, so that neither cyamelide nor free ammonia could be present. On the addition of strong nitric acid, there was a copious evolution of gas, and no precipitate of urea nitrate was obtained. Silver nitrate gave a pure white precipitate, soluble in nitric acid, and also in boiling water, from which crystals were deposited on cooling. These reactions all tended to show that the substance was ammonium cyanate free from admixture of the impurities met with by Liebig and Wöhler, and analysis served to confirm this conclusion.

0.0607 gave 0.0441  $\text{CO}_2$  and 0.0382  $\text{H}_2\text{O}$ .  $\text{C} = 19.8$ ;  $\text{H} = 7.0$ .

0.0351 „ 13.80 c.c. moist nitrogen at  $11.5^{\circ}$  and 760 mm.  $\text{N} = 46.8$ .

$\text{CH}_4\text{ON}_2$  requires  $\text{C} = 20.0$ ;  $\text{H} = 6.7$ ;  $\text{N} = 46.7$  per cent.

The ammonia in the ammonium radicle of the substance was estimated by adding a weighed portion to excess of silver nitrate (whereby silver cyanate and ammonium nitrate were produced),

filtering, and distilling the filtrate with caustic soda, the ammonia evolved being collected in a known quantity of hydrochloric acid, and determined by titration in the ordinary way.

0.1026 yielded ammonia which neutralised 17.08 c.c. of  $N/10$  acid.  
 $\text{NH}_4\text{CNO}$  requires  $\text{NH}_4 = 30.0$ ; found 30.0 per cent.

The amount of the cyanate radicle was estimated by adding a known weight of the substance to excess of decinormal silver nitrate, silver cyanate being precipitated. Although silver cyanate is perceptibly soluble in water, it is almost insoluble in water containing silver nitrate (Walker and Hambly, *loc. cit.*, 747). The precipitate was therefore washed in a Gooch crucible, first with water containing a little silver nitrate, and then with absolute alcohol until the filtrate gave no reaction for silver. The silver cyanate was then dried at  $120^\circ$  and weighed.

0.1235 gave 0.3126  $\text{AgCNO}$ .  $\text{CNO} = 70.9$ .  
 $\text{NH}_4\text{CNO}$  requires  $\text{CNO} = 70.0$  per cent.

These analyses show that the substance obtained by mixing ammonia and cyanic acid in ethereal solution at a low temperature is normal ammonium cyanate free from admixture with other substances.

In order to ascertain if it were not possible to prepare pure ammonium cyanate without the medium of a liquid solvent, the gaseous substances were brought together at the ordinary temperature in a diluted state, so that heating might be avoided as far as possible. A current of dry hydrogen was led through a cooled ethereal solution of cyanic acid, and then by means of a glass tube to the bottom of a large globe. Into the same globe was led a stream of air which had bubbled through strong aqueous ammonia, and had then been dried by passing over quicklime and solid caustic potash. These gases therefore carried into the globe gaseous cyanic acid and ammonia respectively in a dilute condition. The currents were so regulated that the reacting substances were delivered slowly, and as they entered at different parts of the large globe, the process of mixing was very gradual, the ammonium cyanate falling as a sort of snow at the bottom of the globe, and forming vegetative growths round the mouths of the delivery tubes.

After a sufficient quantity had collected, the substance was at once transferred to a desiccator, which was rendered vacuous in order to remove any excess of ammonia or cyanic acid which might cling to the salt. The substance was found, as before, to dissolve in water without residue, and to yield a perfectly neutral solution. It therefore contained neither cyamelide nor free ammonia, and analysis showed that it was free from urea,

0.1818 gave 0.4496 AgCNO. CNO = 69.3.

0.1823 „ 0.4517 AgCNO. CNO = 69.4.

$\text{NH}_4\text{CNO}$  requires CNO = 70.0 per cent.

That the precipitate obtained by the addition of the substance to the silver nitrate solution was in reality silver cyanate, was proved by converting the silver salt in the Gooch crucible directly into chloride by means of hydrochloric acid, and weighing the silver chloride thus produced.

0.4517 silver salt gave 0.4297 AgCl. Ag = 71.6.

AgCNO requires Ag = 72.0 per cent.

It thus appears that pure ammonium cyanate may be prepared by the union of gaseous ammonia and cyanic acid, if care be taken that the heat produced by their combination does not raise the temperature of the product to the point at which it is transformed into urea.

The solid cyanate, when prepared from the gases, presents under the microscope the aspect of very fine needles which show double refraction when examined with a polarising apparatus. It is very readily soluble in water, and the solution, when evaporated, leaves a residue of urea. On heating in a capillary melting point tube, it contracts visibly at a temperature somewhat above  $60^\circ$  and melts suddenly at a temperature in the neighbourhood of  $80^\circ$ , the exact point depending on the rate of heating and on the tightness with which the substance is packed in the tube. The fused mass, however, speedily resolidifies, and does not melt again until a temperature of  $128$ – $130^\circ$  has been reached. The contraction at  $60^\circ$  indicates incipient conversion into urea. At  $80^\circ$ , the transformation takes place so rapidly that enough heat is evolved to fuse the urea produced, the second melting point of  $130^\circ$  being that of urea. During the first fusion, a small quantity of gas is invariably evolved, and when the experiment was repeated on a larger scale the gas was found to be ammonia. It was noted also that although the original ammonium cyanate was completely soluble in water, the product after transformation left a slight insoluble residue which was apparently cyamelide. This production of small quantities of ammonia and cyamelide constantly accompanies the transformation of solid ammonium cyanate into urea, and sufficiently explains the origin of the impurities obtained by Liebig and Wöhler, as well as their inference that the substance produced by the union of gaseous ammonia and cyanic acid is a basic ammonium cyanate.

A quantitative experiment was made in order to determine the amount of ammonia given off during the conversion of the solid cyanate into urea. A Lunge nitrometer was filled with dry mercury up to the Greiner and Friedrich stopcock with which it was provided.

There was then connected directly to the capillary tube, by means of a small piece of thick-walled rubber tubing, a bulb-tube which contained 1 gram of solid ammonium cyanate. By raising and lowering the mercury reservoir, with suitable manipulation of the stopcock, the bulb was rendered vacuous, and the mercury finally permitted to run back so as to fill it. The bulb was then heated in water at 95°, and after about a minute gas was vigorously evolved. When the transformation was complete, the mercury levels were adjusted and the volume of gas read off, the capacity of the bulb and capillary having previously been determined; 1 c.c. of water was then introduced into the nitrometer, and in this the gas dissolved completely. The volume of ammonia obtained in this experiment and reduced to normal conditions was 11.4 c.c., corresponding to 0.0086 gram. The quantity of dry cyanate which would produce this amount of ammonia is 0.030 gram, so that we may say that 3 per cent. of the cyanate on transformation is decomposed with production of ammonia, the rest of the molecule being probably converted into cyanuric acid and cyamelide.

For purposes of comparison with the ammonium cyanate prepared in aqueous solution by Walker and Hambly, a determination of the rate of transformation into urea was made. A decinormal solution of the pure ammonium cyanate was prepared, and the progress of its conversion into urea followed by means of silver titration as previously described (Trans., 1895, 67, 746). The temperature of experiment was 50.2°.

$t$ .	$x$ .	$A-x$ .	$\frac{1}{t} \cdot \frac{x}{A-x}$ .
55	4.94	17.96	0.00500
97	7.44	14.46	0.00496
186	10.74	12.16	0.00475
298	13.64	9.26	0.00494

Mean..... 0.00491

The mean value for the expression  $\frac{1}{t} \cdot \frac{x}{A-x}$  here observed is identical with that calculated for the same temperature from the formula used to express the results of all the experiments in aqueous solution (Walker and Hambly, *loc. cit.*).

#### *Thermochemistry of Ammonium Cyanate.*

From the displacement by change of temperature of the point of equilibrium between ammonium cyanate and urea in aqueous solution, Walker and Kay (*loc. cit.*, p. 507) were able to calculate roughly the heat of transformation into urea of the cyanate in the form of ions.

They found that the heat of transformation was positive, and of the dimensions of 50  $K$  per gram-molecule,  $K$  being equal to 100 cal. It was of interest, therefore, to determine directly, if possible, the heat of transformation of solid ammonium cyanate, and also its heat of solution, for from these data and the known heat of solution of urea the heat of transformation of the dissolved cyanate can be calculated.

The accurate determination of the heat of transformation of the solid cyanate into urea presents considerable difficulty, inasmuch as the conversion only takes place readily at about  $80^{\circ}$ , and therefore necessitates somewhat complicated apparatus. Since, however, the actual transformation is always accompanied by secondary decompositions, an accurate determination for the pure reaction is plainly impossible, so that we contented ourselves with experiments made by means of simple apparatus, which afforded numbers probably within 5 per cent., and certainly within 10 per cent., of the real value.

The calorimeter consisted of two beakers, one within the other, the inner one being supported on cork prisms, and kept from contact with the outer beaker by means of cardboard rings. These beakers were introduced into a double-walled steam oven and rested on a piece of asbestos, which was in turn supported by a stage made of glass tubing. Through the hole in the top of the oven were introduced a thermometer, a stirrer, and a wide glass tube for delivering the experimental substances, all three projecting into the inner vessel after passing through corresponding apertures in the cover of the outer beaker. The most suitable calorimetric liquid we found to be melted paraffin wax, about 50 grams of which were contained in the inner vessel. The thermometer employed was divided into tenths of a degree, so that hundredths of a degree could be estimated.

To perform an experiment, the water in the walls of the steam oven was kept at a constant level and in steady ebullition until the temperature registered by the thermometer in the paraffin became constant, which it usually did in the neighbourhood of  $96^{\circ}$  after about 5 hours. A weighed quantity of mercury of known temperature was then rapidly introduced through the wide glass tube into the inner vessel, and the course of the thermometer was followed for about 10 minutes. From the readings, the weight, specific heat, and original temperature of the mercury, the amount of heat taken up by the latter could be easily calculated. Thus 60 grams of mercury at  $14.70^{\circ}$ , when introduced into the beaker containing 49 grams of paraffin wax, lowered the temperature from  $95.80^{\circ}$  to a minimum of  $92.12^{\circ}$ . The mercury had therefore absorbed 154 cal. from the calorimeter and had thereby lowered the temperature  $3.68^{\circ}$ , or making due allowance for the rate of heating,  $3.86^{\circ}$ . A similar experiment

made with the same weight of paraffin showed that 152 cal. absorbed by the mercury lowered the temperature of the calorimeter  $3.88^{\circ}$ .

After preliminary experiments had shown the approximate value of the heat of transformation of ammonium cyanate, a quantity of this material was chosen so that, by its conversion into urea, it would give to the calorimeter about as much heat as the mercury had absorbed in the previous experiments, all other conditions remaining the same. The weighed quantity of cyanate was compressed into the form of a short cylinder in order that it might be easily introduced through the glass tube into the calorimetric vessel. After the cyanate had entered the paraffin, the thermometer at first fell, owing to the heat required to raise the temperature of the cyanate to the transformation point; thereafter, the rise was rapid, a maximum temperature being soon reached. By making use of the previous experiments with mercury, the total amount of heat supplied to the calorimeter could be easily calculated, allowance being made for the rate of cooling from the thermometric observations. The heat of transformation was greater than this amount by the quantity of heat necessary to raise the temperature of the cyanate, or its transformation products, from the atmospheric temperature to the maximum temperature observed. In calculating this quantity, it was assumed that the cyanate had the same specific heat as its chief transformation product, urea. From the experiments, it appears that the *molecular heat of transformation* of solid ammonium cyanate into solid urea is  $49\ K$ , the chief source of uncertainty lying in the unknown thermal change which accompanies the decomposition of 3 per cent. of the cyanate with formation of ammonia.

Another set of experiments made with a modified apparatus in which a Victor Meyer toluene bath was used instead of a steam oven, yielded a mean value of  $48\ K$  as the molecular heat of transformation of the cyanate.

If we accept  $49\ K$  as the heat of conversion of the cyanate into urea, it follows that the *molecular heat of formation* of solid ammonium cyanate from its elements is  $738\ K$ , since  $787\ K$  is the molecular heat of formation of solid urea, and this must be greater than that of the cyanate by the observed heat of transformation.

In determining the *heat of solution* of ammonium cyanate, the calorimeter chosen was of the simple form described by Nernst (*Zeit. physikal. Chem.*, 1888, 2, 23). The amount of water employed was 200 grams, the water equivalent of the calorimeter being 11.8 grams, as calculated from the weight of materials, and 11 grams as found by direct experiment. The substance whose heat of solution was to be investigated was enclosed in a thin-walled glass bulb weighted with

mercury so as to sink in the water of the calorimeter. When the temperature had become constant, the bulb was broken and the course of the thermometer observed.

In order to test the apparatus, the heat of solution of urea was first determined. The values obtained were  $-36.1$ ,  $-36.6$ , and  $-36.3 K$  for the gram-molecule, in good accordance with Rubner's number of  $-36.8 K$ .

For the *molecular heat of solution* of ammonium cyanate, the mean of two concordant experiments was  $-62.3 K$ , the strength of the resulting solution being about one-twentieth normal. This number is somewhat greater than we had anticipated, being in excess of the corresponding value for potassium cyanate, namely,  $-52 K$ , in opposition to the general rule that the potassium salts have greater heats of solution than the ammonium salts of the same acids. The divergence cannot be explained by the assumption that a portion of the cyanate is transformed into urea during the progress of the experiment. The portion so transformed could at most have reached only 2 per cent. of the total, and the thermal effect of the transformation would have been to diminish the heat of solution instead of to increase it.

The heat of transformation of the cyanate into urea in aqueous solution may be calculated from the corresponding value for the solid substance as follows. We may pass from solid ammonium cyanate to dissolved urea in two ways, namely, by transforming the cyanate in the solid state and then dissolving the urea, or by dissolving the cyanate and then transforming it in aqueous solution. The total heat effect must be the same in both cases, so that we obtain the equation :

Heat of transformation of solid cyanate + heat of solution of urea =

Heat of solution of cyanate + heat of transformation in solution,  
or, substituting the numerical values for the gram molecular weight,

$$49 K + (-36 K) = -62 K + x,$$

whence  $x = 75 K$ .

This value for the heat of transformation of the gram-molecule of ammonium cyanate in aqueous solution is considerably in excess of the value  $50 K$  calculated from the displacement of the equilibrium point with change of temperature. This latter value, however, can only be taken as indicating the sign and dimensions of the heat change, since in the calculation it was assumed that the transformation was pure, instead of being complicated, as is actually the case, with subsidiary actions which affect the accuracy of the deduction, and, secondly, that the cyanate was fully dissociated at the dilutions considered, an assumption which is only approximate. The number  $75 K$  must there-

fore be accepted as a considerably closer approximation to the true value than the number 50  $K$ , since it is affected by much smaller sources of error.

It may be noted that the value observed for the heat of transformation of the solid cyanate is sufficiently great to account for the fusion of the urea which occurs when the transformation takes place suddenly at about 80°. At this temperature, the transformation proceeds at such a rate that the heat evolved cannot all escape by conduction; the temperature therefore rises and the action is accelerated until it proceeds almost instantaneously, with sudden evolution of so much heat that the temperature is raised above the melting point of urea, the heat of fusion of urea being probably less than  $-25 K$ .

#### *Rate of Transformation into Urea.*

It has been already stated that the substance obtained by Liebig and Wöhler remained unchanged for a week in an atmosphere of dry ammonia, whilst in the course of two days it was almost entirely converted into urea when exposed to the air, ammonia being continually evolved during the transformation. Liebig and Wöhler were apparently of opinion that the presence or absence of ammonia was the determining circumstance in the conversion. This, however, is not the case, as we have found that moisture plays the chief part in determining the rate of transformation at moderate temperatures. Exposed to a moist atmosphere, the cyanate, as Liebig and Wöhler observed, is converted into urea in the course of a few days. If left in a desiccator over sulphuric acid, the cyanate in the same length of time remains practically unchanged; and in an exhausted tube in presence of phosphoric oxide the cyanate shows little sign of alteration even after several months.

Two tubes were prepared, one with dry (but not specially dried) cyanate, the other with the same material and a minute trace of moisture introduced from the end of a fine capillary. These tubes were sealed off and heated at the same temperature for the same length of time. In the tube containing the added moisture, 27 per cent. of the cyanate had been transformed into urea, whilst in the other tube only 2 per cent. had undergone transformation.

As might be expected, temperature has a great influence on the rate of transformation. It has already been indicated that the transformation proceeds at a noticeable rate when the temperature reaches 60° for then a distinct diminution in volume is visible when the substance is contained in a capillary tube. An experiment with ordinary dry cyanate showed that in the course of two hours 80 per cent. of the cyanate was converted into urea at that temperature.



In order to ascertain the effect of temperature on the rate of transformation of carefully dried cyanate, the following experiment was made. Four small tubes were charged with weighed quantities of cyanate and placed in tubes which were slightly wider than themselves and contained a layer of phosphoric oxide on the bottom. These outer tubes were then rendered vacuous and sealed off. After ten days, the tubes, without being opened, were heated at various temperatures, either in thermostats or in boiling liquids, for such lengths of time as preliminary experiments had shown would bring about approximately the same extent of transformation. The times required for the conversion of 3.5 per cent. of the cyanate into urea are exhibited in the following table :

Temperature.	Time in hours.
33°	50
40	19
45	7
57	1.1

The dried cyanate, like the freshly prepared material, passed rapidly into urea with fusion when the temperature was raised to a little over 80°.

The rate of transformation we found to be by no means proportional to the amount of cyanate present, as the following figures indicate. The cyanate used was contained in vacuous tubes and dried for five days over phosphoric oxide in the manner described above, the temperature of transformation being 57°.

Time in hours.	Percentage transformed.
1	5.4
2	19.4
5	58.6
10	95.1

In the first hour, only 5.4 \* per cent. was converted into urea, whilst in the second hour 14 per cent. of the original amount, or 14.7 per cent. of the amount remaining after the first hour, underwent transformation. Between the second and fifth hours there was transformed hourly, on the average, 16 per cent. of the amount of cyanate which remained at the beginning of the time, and in the last period of five hours there was an hourly average transformation of 18 per cent. of the amount of cyanate present at the commencement of the period. There are thus evidences of a gradual acceleration of the action as it progresses. This we might expect, since the transformation is one in a condensed two-phase system. The action is probably not uniform

\* This number is greater than the corresponding number in the temperature experiments quoted above, on account of less perfect drying.

through the whole mass, but proceeds from definite points or nuclei, the rate increasing as the surface of contact between the two phases increases, as it does in the crystallisation of an over-cooled liquid, or the conversion of one crystalline modification into another.

So far as we have observed, there is no tendency to the reverse transformation of urea into ammonium cyanate in the solid state. After being heated for a long time in a vacuous tube at  $110^{\circ}$ , dry urea was found to be unchanged, dissolving completely in water with formation of a perfectly neutral solution which gave no precipitate with silver nitrate. After heating for 6 hours at  $129^{\circ}$ , that is, just below its melting point, it was found to have slightly decomposed with production of ammonia, but the presence of cyanate could not be proved in the residue. Whether the ammonia and cyanuric acid produced by heating urea to a still higher temperature are entirely the decomposition products of urea and biuret, or are in part derived from ammonium cyanate into which a portion of the urea may have been transformed, is a point to which we can at present give no definite answer.

Waddell (*J. Physical Chem.*, 1898, 2, 525) has shown that solid ammonium thiocyanate does not suffer transformation into thiourea below a temperature of  $110^{\circ}$ . When fused, however, at temperatures of  $150^{\circ}$  and over, it is gradually converted into thiourea, the rate of transformation rising rapidly with the temperature. In this case, the transformation is not complete, equilibrium being attained when the fused mass contains 80 per cent. of thiourea and 20 per cent. of thiocyanate. The existence of a similar state of equilibrium between urea and ammonium cyanate cannot be ascertained, owing to the decomposition which these substances suffer when in the fused state. There can of course be no such equilibrium between the solids, for when two mutually convertible solids are in contact with each other, there is no real equilibrium between them except at one definite temperature, the transition or inversion point, at which temperature they may be brought together in any proportion without either undergoing change. In the fused state, on the other hand, the substances are miscible, and thus form but one phase instead of two, the system thereby gaining an additional degree of freedom, so that equilibrium may be attained at any temperature, the composition of the system changing according as the temperature varies. What the transition point of ammonium cyanate and urea may be, we are not in a position to determine. All that can be said is that it is above  $80^{\circ}$ , and in all probability very far above that temperature.

*Substituted Ammonium Cyanates.*

When dry ethylamine was gradually mixed with the vapour of cyanic acid, the two substances united to form a light, colourless powder, the solution of which, in water, gave a precipitate of silver cyanate when brought into contact with silver nitrate solution. The white powder, therefore, consisted, in part, at least, of ethylammonium cyanate. On standing for some time, it showed indications of lessening in bulk, and eventually it liquefied. The liquid, however, soon set to a solid mass, which, when dissolved in water, gave no precipitate with silver nitrate. The phenomena encountered here are consequently similar to those met with in the case of ammonium cyanate, the only difference being that the ethylammonium cyanate is rapidly converted into ethylurea at a much lower temperature than suffices for the rapid transformation of ammonium cyanate.

An ethereal solution of aniline, when mixed with an ethereal solution of cyanic acid, gave no immediate precipitate, but the solution deposited a crystalline substance on standing for some time. The crystals which separated, however, did not behave as phenylammonium cyanate, but as phenylurea. A similar result was obtained with *p*-toluidine as base; the crystalline substance which separated from the ethereal solution on standing proved to be *p*-tolylurea, and not *p*-tolylammonium cyanate.

These substituted ammonium cyanates therefore pass much more readily into the corresponding ureas than ammonium cyanate itself.

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IV.—*Etherification of Derivatives of  $\beta$ -Naphthol.*

By WILLIAM A. DAVIS.

IN the following pages, an account is given of the etherification of derivatives of  $\beta$ -naphthol by heating the naphthol with a mixture of alcohol and sulphuric acid (Henriques, compare Gattermann, *Annalen*, 1887, 244, 72). It is shown that, whereas  $\beta$ -naphthol yields an almost theoretical amount of ether, most of its derivatives can only be very partially etherified.

As no action occurs at the ordinary temperature, in the first series of experiments a mixture of 2 grams of purified naphthol with 2 grams of the alcohol and 0.8 gram of sulphuric monohydrate was gently boiled during  $6\frac{1}{2}$  hours on the sand-bath in a test-tube attached to a condenser.

To free the ether from unchanged naphthol, an excess of dilute caustic soda was then added, and the mixture gently warmed, a preliminary experiment having shown that this could be done without hydrolysis or dissolution of the ether taking place. The ether was collected on a tared filter-paper, which had previously been exposed in a weighing bottle in a vacuum until its weight was constant, and after being thoroughly washed, was dried in a vacuum desiccator and weighed. The results obtained are given in Table I.

Owing to a considerable proportion of the alcohol being converted into ethyl ether by the action of the sulphuric acid at the temperature at which the mixture boiled, it was generally observed that the latter separated, after about 3 hours, into two layers, of which the upper contained the alcohol and sulphuric acid, whilst the lower consisted of the naphthyl ether and unchanged naphthol. Owing to this separation, little etherification occurred after the third hour. It was found, however, that at  $100^{\circ}$ , whilst the formation of ethyl ether was largely prevented, that of the naphthyl ether was not interfered with; in addition, the disturbing influence which is undoubtedly exercised on the etherification by varying the rate of ebullition was entirely excluded. Table II gives the results obtained at  $100^{\circ}$ . In these experiments, the mixture was heated during a much longer period than in the experiments recorded in Table I, and a definite limit of etherification was attained; it is doubtful whether this limit had been reached in the first series of experiments, as will appear on comparing the two sets of results. The method of heating at first adopted was to surround the tube containing the etherification mixture with boiling water, but the results obtained were, in some cases, vitiated by moisture permeating the cork; subsequently the lower portion only of the tube was heated by passing it through a cork fitted into the neck of a steam-bath constructed from a sheet-iron can by soldering six short tubes 1 inch in diameter round the central neck. A condenser, fitted to the central neck, served to keep the volume of water in the can practically constant.

Table III gives the results of experiments carried out at  $100^{\circ}$ , using methyl instead of ethyl alcohol; these values are probably not quite so trustworthy as those of Table II, for two reasons. First, the mixture used boiled below  $100^{\circ}$ , and a considerable decrease in its amount occurred owing to the formation of methyl ether; secondly, a small proportion of the naphthyl ether sublimed, and thus a change in the condition of equilibrium was introduced. The latter circumstance probably accounts for the fact that the amounts of ether obtained with methyl are higher than those obtained with ethyl alcohol; in experiment 2, especially, much sublimation occurred. The results obtained with 3'-bromo-2-naphthol are possibly slightly higher than the true

values, owing to the fact that 3'-bromo-2-methoxynaphthalene does not melt below 100° when warmed with dilute caustic soda, so that small quantities of unchanged naphthol probably remained occluded; moreover, much of the product sublimed. The alcohol used boiled at 66·0—66·5° under 759 mm. pressure.

Similar experiments were made with propyl alcohol (b. p. 96·25—97° under 747·5 mm. pressure); the results are given in Table IV. In the case of 1:3'-dibromo-2-naphthol, resinous substances insoluble in caustic soda were formed owing to the occurrence of secondary change.

TABLE I.—*Etherification at the boiling point.*

No. of experiment.	Naphthol.	Time in hours.	Percentage yield of ether.	M.p. of product weighed.	M.p. of pure ether.
1	$\beta$ -Naphthol.....	6	83·0	36°	37·5°
2	"	6½	84·1	37	37·5
3	3'-Bromo-2-naphthol .....	6½	68·0	77—78	80
4*	"	6½	69·7	76—77	80
5	1-Bromo-2-naphthol .....	6½	9·7	54—56	66
6	"	"	20·2	54—58	66
7	"	"	23·1	55—58	66
8	"	"	2·1	64—65	66
9	"	"	4·1	62—64	66
10*	"	"	5·0	64—65	66
11	1-Chloro-2-naphthol .....	"	8·1	55—56	58
12	"	"	10·0	55—56	58
13*	1-Iodo-2-naphthol .....	"	resin formed.		
14	1:3'-Dibromo-2-naphthol .....	8	9·4	74—76	94
15	"	6½	7·6	79—80	94
16	"	6½	9·7	79	94
17	"	6½	1·4	89	94
18	"	6½	1·25	89—90	94
19	"	6½	0·7	88	94
20	"	6½	3·4	65—70	94
21†	"	6½	0·0	—	—
22†	"	6½	0·0	—	—
23	1-Chloro-3'-bromo-2-naphthol.	6½	3·9	65—67	77
24	"	6½	2·3	75	77
25	"	6½	0·9	74	77
26*	"	6½	1·5	74	77
27	1:3-Dichloro-2-naphthol.....	6½	0·0	—	—
28*	"	6½	0·0	—	—
29	Tribromo-2-naphthol (m.p. 155°) .....	6½	0·0	—	—
30	1-Nitro-2-naphthol.....	6½	0·87	96—98	104

In all experiments except those marked \* and †, the proportions in grams were—naphthol:ethyl alcohol:sulphuric acid = 2:2:0·8; in those marked with an asterisk, the *molecular* proportions were the same as in the etherification of  $\beta$ -naphthol, namely, 1 mol. naphthol:3·12 mols. alcohol:0·59 mol. acid. In two experiments, Nos. 21 and 22,

the proportion of sulphuric acid was the same as in the experiments with  $\beta$ -naphthol, but 2 grams of alcohol were used. Unsatisfactory results were obtained in experiments 5, 6, 7, 14, 15, and 16 with 1-bromo- and 1:3'-dibromo-2-naphthol, owing to the fact that the mixture was boiled too rapidly, this giving rise to compounds insoluble in dilute caustic soda, which seriously interfered with the purity of the ether. Moreover, on filtering the dilute, alkaline solution of the unchanged naphthol, oxidation apparently occurred, and the solution became purple in colour, depositing a finely-divided purple or brownish powder in the pores of the filter paper, thus preventing further filtration. In the later experiments (Nos. 8, 9, 10, 17, 18, 19), the ebullition was carefully regulated and the filtration hastened by using a filter-pump; under these conditions, the ether weighed was nearly pure. The melting points given in the table serve to indicate the degree of purity of the products weighed.

TABLE II.—*Etherification at 100°.*

*Proportions*:—Naphthol:ethyl alcohol:sulphuric acid = 2:2:0·8 grams.

No. of experiment.	Naphthol.	Time in hours.	Percentage yield of ether.	M.p. of product weighed.	M.p. of pure ether.
1	$\beta$ -Naphthol .....	2½	73·6	37—38°	37·5°
2	" .....	3½	83·9	37	37·5
3	" .....	11	90·5	"	"
4	" .....	15½	91·2	"	"
5	" .....	20	89·1	"	"
6	3'-Bromo-2-naphthol .....	20	88·7	79	80
7*	1-Bromo-2-naphthol .....	6½	3·2	62—64	66
8	" .....	15	15·2	62—64	66
9	" .....	20	17·0	63—64	66
10*	1-Chloro-2-naphthol .....	6½	0·5	55—56	58
11*	" .....	15½	2·1	56	"
12	" .....	20	9·3	55—56	"
13	" .....	25	8·4	56	"
14*	1:3'-Dibromo-2-naphthol .....	11	0·36	—	94
15*	" .....	16½	1·3	82—85	"
16	" .....	20	6·0	84—86	"
17	1-Chloro-3'-bromo-2-naphthol .....	6½	0·0	—	77
18	" .....	16	1·9	67—76	77
19	1:3-Dichloro-2-naphthol .....	20	0·0	—	—
20	1-Nitro-2-naphthol .....	20	0·0	—	104
21	1-Nitro-3-chloro-2-naphthol .....	20	0·0	—	—
22	1:3:4-Trichloro-2-naphthol .....	20	0·0	—	—

In the experiments marked \*, the mixture was heated in boiling water; in all others, the steam-bath was used.

TABLE III.—*Methylation at 100°.*

*Proportions:* Naphthol : methyl alcohol : sulphuric acid = 2·0 : 2·0 : 0·8 grams.

No. of experiment.	Naphthol.	Time in hours.	Percentage yield of ether.	M. p. of product weighed.	M. p. of pure ether.
1	$\beta$ -Naphthol.....	20	91·15	71—72°	72°
2	" .....	20	95·9	71	72
3	" .....	20	91·3	71—72	72
4	1-Bromo-2-naphthol .....	20	21·2	80	82—83
5	" .....	20	22·4	80—81	82—83
6	3'-Bromo-2-naphthol .....	18½	98·7	104	105
7	" .....	20	97·1	104	105
8	1-Chloro-2-naphthol .....	"	7·45	60	68
9	1 : 3'-Dibromo-2-naphthol .....	"	5·4	73—76	100
10	1 : 3'-Chlorobromo-2-naphthol .....	"	0·0	—	—
11	1-Nitro-2-naphthol .....	"	0·0	—	126

TABLE IV.—*Propylation at 100°.*

*Proportions:*—Naphthol : propyl alcohol : sulphuric acid = 2 : 2 : 0·8 grams.

No. of experiment.	Naphthol.	Time in hours.	Percentage yield of ether.	M. p. of product weighed.	M. p. of pure ether.
1	$\beta$ -Naphthol.....	12	94·5	38°	39·5°
2	" .....	20	93·3	37—38	39·5
3	3'-Bromo-2-naphthol .....	20	93·8	62	63·5
4	" .....	20	92·0	62	63·5
5	1-Bromo-2-naphthol .....	20	12·7	29	35—36
6	" .....	20	12·9	23—28	"
7	1-Chloro-2-naphthol .....	20	0·75	oil	—
8	" .....	20	0·0	—	—
9	1 : 3'-Dibromo-2-naphthol.....	16	2·6	45°, dirty	75
10	" .....	20	decomposition		
11	1-Chloro-3'-bromo-2-naphthol.	20	0·58	56	60·5
12	1 : 3-Dichloro-2-naphthol.....	20	0·0	—	—
13	1-Nitro-2-naphthol.....	20	0·0	—	—

### *$\beta$ -Naphthyl Methyl Ethers.*

3'-Bromo-2-methoxynaphthalene,  $C_{10}H_7Br \cdot OMe$ , prepared by heating a mixture of 5 grams of 3'-bromo-2-naphthol (Armstrong and Davis, Proc., 1896, 12, 231) and 5 grams of methyl alcohol during 10 hours at 100°, is sparingly soluble in alcohol, moderately so in benzene, ethyl

acetate, chloroform, or acetone, and crystallises from acetic acid in balls of small, white needles; it melts at  $105^{\circ}$ .

0.2342 gave 0.1875 AgBr. Br = 34.07.

$C_{11}H_9OBr$  requires Br = 33.74 per cent.

1-Bromo-2-methoxynaphthalene,  $C_{10}H_7Br \cdot OMe$ , was prepared by heating 4 grams of 1-bromo-2-naphthol with 2.7 grams of methyl iodide, 1.4 grams of potassium hydroxide, and 10 grams of methyl alcohol during 5 hours in a sealed tube at  $100^{\circ}$ ; it crystallises best from light petroleum, forms thin, lustrous plates, and melts at  $82.5^{\circ}$ .

0.1643 gave 0.1290 AgBr. Br = 33.42.

$C_{11}H_9OBr$  requires Br = 33.74 per cent.

1-Chloro-2-methoxynaphthalene,  $C_{10}H_7Cl \cdot OMe$ , prepared in a similar manner, crystallises from alcohol in thin, colourless plates, and melts at  $68^{\circ}$ .

0.2100 gave 0.1571 AgCl. Cl = 18.50.

$C_{11}H_9OCl$  requires Cl = 18.41 per cent.

1:3'-Dibromo-2-methoxynaphthalene,  $C_{10}H_5Br_2 \cdot OMe$ .—When 5 grams of 1:3'-dibromo-2-naphthol are heated with 2.5 grams of methyl iodide, 1.4 grams of potassium hydroxide and 12 grams of methyl alcohol in a sealed tube during 6 hours at  $100^{\circ}$ , a portion of the naphthol is not acted on, and only about 50 per cent. of the theoretical quantity of 1:3'-dibromo-2-methoxynaphthalene is obtained; it crystallises best from alcohol in small, nearly colourless plates and melts at  $100^{\circ}$ .

0.1316 gave 0.1552 AgBr. Br = 50.20.

$C_{11}H_5OBr_2$  requires Br = 50.62 per cent.

1-Chloro-3'-bromo-2-methoxynaphthalene,  $C_{10}H_6ClBr \cdot OMe$ , prepared in a similar manner from 1-chloro-3'-bromo-2-naphthol, crystallises from hot alcohol in thin, colourless plates, which are at first transparent, but become slightly opaque as the solution cools, possibly owing to a change in crystalline form; it melts at  $92.5^{\circ}$ .

0.1428 gave 0.1747 AgCl + AgBr. AgCl + AgBr = 122.33.

$C_{11}H_6OClBr$  requires AgCl + AgBr = 122.00 per cent.

### *$\beta$ -Naphthyl Ethyl Ethers.*

1-Bromo-2-ethoxynaphthalene,  $C_{10}H_7Br \cdot OEt$ , is best prepared by adding bromine (1 mol.) drop by drop to a solution of  $\beta$ -ethoxynaphthalene in glacial acetic acid, but is also formed by ethylating 1-bromo-2-naphthol; it crystallises from light petroleum in colourless plates and melts at  $66^{\circ}$ .



*3'-Bromo-2-ethoxynaphthalene*,  $C_{10}H_6Br \cdot OEt$ , is best prepared by heating a mixture of 5 grams of 3'-bromo-2-naphthol, 5 grams of ethyl alcohol, and 2.0 grams of sulphuric monohydrate during 6 hours at  $100^\circ$ ; it crystallises from alcohol in colourless plates, melts at  $80^\circ$ , and is easily soluble in benzene, acetic acid, chloroform, ether, ethyl acetate, or light petroleum.

0.1382 gave 0.1041 AgBr. Br = 32.05.

$C_{12}H_{11}OBr$  requires Br = 31.88 per cent.

On one occasion, a mixture of 20 grams of 3'-bromo-2-naphthol with 20 grams of ethyl alcohol and 8 grams of sulphuric acid was, by an oversight, boiled more vigorously than was intended, and nearly the whole of the alcohol evaporated; as a consequence a considerable quantity of 3'-bromo-2-naphtholdisulphonic acid (Armstrong and Davis, Proc., 1896, 12, 231) was formed. On removing this by adding water, a small quantity of a heavy oil remained undissolved; on washing this with a little alcohol, it solidified to a dark, greyish powder. The alcoholic washings were poured into water and the precipitate obtained crystallised from light petroleum containing a small quantity of benzene, when small, colourless needles separated melting at  $125^\circ$ ; these were insoluble in aqueous caustic soda and therefore did not consist of unchanged 3'-bromo-2-naphthol, which melts at  $127^\circ$ , but the quantity of substance obtained was insufficient to determine its nature by an analysis. The greyish powder left undissolved by the alcohol was crystallised from glacial acetic acid; it separated in colourless plates melting at  $169^\circ$  to a deep red liquid; after crystallisation, it became very sparingly soluble in glacial acetic acid and was insoluble in aqueous caustic soda. On analysis, the following numbers were obtained:

0.2140 gave 0.1813 AgBr. Br = 36.06 per cent.

0.2768 „ 0.2327 AgBr. Br = 35.79 „

These results and the properties of the substance suggested that it was somewhat impure di-3'-bromo-2-naphthyl ether,  $(C_{10}H_6Br)_2O$ . The quantity of substance obtained, however, was so small as to preclude further purification, but the view as to its nature was confirmed by a comparison with the dinaphthyl ether.

*Di-3'-bromo-2-naphthyl ether* is prepared by boiling 2 grams of 3'-bromo-2-naphthol with 30 grams of 50 per cent. sulphuric acid during 12 hours in a reflux apparatus; the yield in these circumstances is small, most of the naphthol being recovered unchanged; it crystallises from glacial acetic acid in colourless plates and melts at  $170$ – $171^\circ$ , the melting point being unchanged by mixing it with the substance melting at  $169^\circ$  which was believed to be identical with it.

0.0954 gave 0.0824 AgBr. Br = 36.86.

$C_{20}H_{12}O_2Br_2$  requires Br = 37.22 per cent.

1-Chloro-2-ethoxynaphthalene,  $C_{10}H_6Cl \cdot OEt$ , prepared by heating 1-chloro-2-naphthol (2 grams) with ethyl bromide (1.3 grams), caustic potash (1.0 gram), and absolute alcohol (12 grams) during 3 hours at  $100^\circ$ , crystallises from alcohol in beautiful, colourless leaflets and melts at  $58^\circ$ ; it is easily soluble in benzene or light petroleum, and very soluble in chloroform, ethyl acetate, or acetone.

0.2051 gave 0.1414 AgCl. Cl = 17.04.

$C_{12}H_{11}OCl$  requires Cl = 17.17 per cent.

1:3': Dibromo-2-ethoxynaphthalene,  $C_{10}H_5Br_2 \cdot OEt$ , is best prepared by gradually adding bromine (2 mols.) to  $\beta$ -ethoxynaphthalene dissolved in four times its weight of glacial acetic acid, and subsequently warming at  $100^\circ$ ; it crystallises from light petroleum in beautiful, lustrous needles and melts at  $94^\circ$ . Its structure follows from its being formed when 1:3'-dibromo-2-naphthol is heated with the theoretical quantity of ethyl bromide and caustic potash in absolute alcohol during 5 hours at  $100^\circ$ .

0.1540 gave 0.1756 AgBr. Br = 48.52.

$C_{12}H_{10}OBr_2$  requires Br = 48.49 per cent.

1-Chloro-3'-bromo-2-ethoxynaphthalene,  $C_{10}H_5ClBr \cdot OEt$ , obtained by heating 1-chloro-3'-bromo-2-naphthol with ethyl bromide (2.5 grams), sodium hydroxide (1 gram), and absolute alcohol (15 grams) in a sealed tube for 6 hours at  $100^\circ$ , crystallises from alcohol or light petroleum in thin, colourless, lustrous, elongated plates and melts at  $77.5^\circ$ ; it is very soluble in benzene, chloroform, ether, acetone, or ethyl acetate.

0.1829 gave 0.2130 AgCl + AgBr. AgCl + AgBr = 116.5.

$C_{12}H_{10}OClBr$  requires AgCl + AgBr = 116.1 per cent.

### *$\beta$ -Naphthyl Propyl Ethers.*

$\beta$ -Propoxynaphthalene, according to Bodroux (*Compt. rend.*, 1898, 126, 840), is formed on heating  $\beta$ -naphthol with propyl iodide and alcoholic potash, but it is best prepared by gently boiling a mixture of  $\beta$ -naphthol (10 grams), propyl alcohol (10 grams), and sulphuric monohydrate (4 grams) during 6 hours. It crystallises best from alcohol in long, colourless needles, and melts at  $39.5^\circ$  as stated by Bodroux.

3'-Bromo-2-propoxynaphthalene,  $C_{10}H_5Br \cdot OPr^a$ , prepared in the same manner as  $\beta$ -propoxynaphthalene, crystallises from hot alcohol in beautiful, thin, transparent plates; before crystallisation is com-

plete, however, white, opaque balls of needles form, whilst these alone are obtained if the amount of alcohol used has been sufficient to prevent crystallisation commencing until the solution has cooled to the atmospheric temperature. The transparent crystals apparently contain alcohol of crystallisation, but this is lost so rapidly on exposure to the air that its amount could not satisfactorily be determined; when the plates are exposed to the air for 6 days, they crumble to powder, and are then free from alcohol, as the following analysis indicates:

0.2051 gave 0.1456 AgBr. Br = 30.21.

$C_{13}H_{13}OBr$  requires Br = 30.18 per cent.

The pure substance melts at  $63.5^\circ$ , but after solidification melts quite sharply at  $56^\circ$  (three determinations), although after 36 hours the melting point has again risen to  $63.5^\circ$ ; it crystallises from glacial acetic acid or light petroleum in small, globular aggregates of white needles and is very soluble in chloroform and ether.

1-Bromo-2-propoxynaphthalene,  $C_{10}H_7Br \cdot OPr^a$ , is best obtained by adding bromine (1 mol.), dissolved in an equal quantity of glacial acetic acid, drop by drop to a cooled solution of  $\beta$ -propoxynaphthalene in glacial acetic acid; an oil separates which is washed with water and caused to solidify by surrounding it with ice; on crystallising from alcohol, nearly colourless, small, prismatic flakes are obtained melting at  $35-36^\circ$ . It is also formed on heating 1-bromo-2-naphthol with propyl bromide (6 grams), caustic potash (2.3 grams), and propyl alcohol during 5 hours at  $100^\circ$ , but the yield is poor (compare 1:3'-dibromo-2-propoxynaphthalene).

0.2032 gave 0.1428 AgBr. Br = 29.85.

$C_{13}H_{13}OBr$  requires Br = 30.18 per cent.

1:3'-Dibromo-2-propoxynaphthalene,  $C_{10}H_5Br_2 \cdot OPr^a$ , is best obtained by gradually adding 2 mols of bromine to  $\beta$ -propoxynaphthalene dissolved in glacial acetic acid; it crystallises from alcohol in well-defined, slightly yellow prisms and melts at  $78^\circ$ . When 1:3'-dibromo-2-naphthol (7.5 grams) is heated with propyl bromide (3.0 grams), caustic potash (2.3 grams), and propyl alcohol (20 grams) in a sealed tube during 7 hours at  $100^\circ$ , a considerable proportion of the naphthol is not acted on, a portion is decomposed, giving rise to resinous products, and the yield of ether is small.

0.1032 gave 0.1134 AgBr. Br = 46.77.

$C_{13}H_{12}OBr_2$  requires Br = 46.50 per cent.

1-Chloro-3'-bromo-2-propoxynaphthalene,  $C_{10}H_6ClBr \cdot OPr^a$ , obtained from 1-chloro-3'-bromo-2-naphthol by the propyl bromide method,

crystallises from alcohol, in which it is moderately soluble, in large, nearly colourless, very thin plates, and melts at  $60.5^{\circ}$ ; on analysis:

0.1848 gave 0.2050 AgCl + AgBr.  $\text{AgCl} + \text{AgBr} = 110.9$ .

$\text{C}_{13}\text{H}_{12}\text{OClBr}$  requires  $\text{AgCl} + \text{AgBr} = 110.6$  per cent.

### *Discussion of Results.*

The results tabulated on pages 35—37 serve to show that a single halogen atom in position 1, contiguous to the hydroxyl group of  $\beta$ -naphthol, has a most remarkable effect in limiting etherification, the effect being least in the case of methyl and greatest in that of propyl alcohol. Chlorine has an even greater effect than bromine, and a nitro-group in position 1 entirely prevents etherification. That the position of the halogen is the main determining cause of its influence is clearly brought out by the fact that 3'-bromo- $\beta$ -naphthol is etherified as easily as the unbrominated naphthol, but it will be seen that, on introducing bromine into position 3' in either 1-chloro- or 1-bromo- $\beta$ -naphthol, the production of ether is considerably diminished.

These results stand in striking contrast to those obtained in the well-known experiments made by Victor Meyer and Sudborough, since extended by others,\* on the etherification of substituted benzoic acids. In the case of benzoic acid, a single group in the ortho-position has little influence, whereas two such groups, if they do not altogether prevent etherification (Cl, Br, I,  $\text{NO}_2$ ), greatly affect either the rate at which it takes place or its extent ( $\text{CH}_3$ , OH, F). Victor Meyer has sought to find an explanation of these facts in stereochemical considerations, and has regarded the influence exercised by various radicles as dependent on their volume; but, strange to say, he has taken *mass* as the measure of volume.†

Such a hypothesis appears to be by no means justified by facts. Thus the order of inhibitive influence of different radicles on the formation of ethereal salts of ortho-substituted benzoic acids appears from Kellas' results to be Cl,  $\text{CH}_3$ , Br, I,  $\text{NO}_2$ ; but the order of the relative weights is  $\text{CH}_3$ , Cl,  $\text{NO}_2$ , Br, I, and that of atomic volumes,  $\text{CH}_3$ , Cl, Br,  $\text{NO}_2$ , I (Graham-Otto, I, 3, 449), or according to Traube (*Annalen*, 1896, 290, 43)  $\text{Cl} = \text{Br} = \text{I}$  (13.2),  $\text{CH}_3$  (19.2),  $\text{NO}_2$  (20). From Goldschmidt's values for the velocity coefficients, the radicles

\* V. Meyer and Sudborough, *Ber.*, 1894, 27, 510, 1580, 3146; Lepsius, *ibid.*, 1635; V. Meyer, *Ber.*, 1895, 28, 182, 1254, 2773, 3197; 1896, 29, 830, 1397; van Loon and V. Meyer, *ibid.*, 839; Goldschmidt, *Ber.*, 1895, 28, 3218, Kellas, *Zeit. physikal. Chem.*, 1897, 24, 221; Wegscheider, *Monatsh.*, 1895, 16, 75; *Ber.*, 1895, 28, 1474, 2535; *Monatsh.*, 1897, 18, 629; Sudborough and Feilmann, *Proc.*, 1897, 13, 241.

† For a discussion of this point, see V. Meyer, *Ber.*, 1895, 28, 126; 1896, 29, 843; Wegscheider, *Ber.*, 1895, 28, 126, *Monatsh.*, 1897, 18, 635.

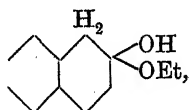
should stand, as regards retarding influence, in the order  $\text{Br}$ ,  $\text{CH}_3$ ,  $\text{NO}_2$ , but in the case of the naphthyl ethers, the order appears from my results to be  $\text{Br}$ ,  $\text{Cl}$ ,  $\text{NO}_2$ . So that the observations of Goldschmidt and of Kellas, as well as my own, are in accord neither with the arrangement by atomic weights nor with that by atomic volumes; consequently, there appears to be a factor governing the etherification of both carboxylic acids and phenols\* of which we are at present in ignorance. Even if we consider, as Sudborough and Feilmann have suggested that the etherification is determined by two factors, (1) the stereochemical influence of the configuration, (ii) the strength of the acid as measured by its affinity constant, we are brought no nearer to an explanation of the extraordinarily great inhibiting influence of a nitro-group compared with that of other groups.†

Wegscheider (*Monatsh.*, 1895, 16, 75, and 1897, 18, 629) has given reasons for considering that, in the etherification of carboxylic acids under the influence of alcohol and concentrated sulphuric acid or hydrogen chloride, an intermediate compound is formed by addition to the carboxyl group, as was originally assumed by Henry (*Ber.*, 1877, 10, 2041), and later work has strengthened this hypothesis (compare Lloyd and Sudborough, *Trans.*, 1899, 75, 580); he has suggested that phenols undergo etherification in a somewhat similar

\* Sudborough and Lloyd (*Trans.*, 1899, 75, 467, 580) give a bibliography of papers dealing with the influence of ortho-substituted groups on the etherification of acids, the hydrolysis of ethereal salts, and of acid chlorides, amides, and nitriles; the results obtained by Küster and Stallberg (*Annalen*, 1894, 278, 207) belong to the same category. Contiguous groups also exert an important influence on the preparation of oximes and phenylhydrazones of aromatic aldehydes and ketones (Kehrmann, *Ber.*, 1888, 21, 3815; 1894, 27, 3344; *J. pr. Chem.*, 1890, [ii], 40, 257; Hantzsch, *Ber.*, 1890, 23, 2769; Feith and Davies, *Ber.*, 1891, 24, 3546; Petrenko-Kritschenko, *Ber.*, 1895, 28, 3203; Baum, *Ber.*, 1895, 28, 3207, V. Meyer, *Ber.*, 1896, 29, 830); the formation of imido-ethers from nitriles (Pinner, *Ber.*, 1890, 23, 2917); and many other more complex interactions (compare Busch, *J. pr. Chem.*, 1895, [ii], 51, 118; 52, 273; 1896, 53, 414; 1897, 55, 356; Jacobson, *Annalen*, 1895, 287, 118; 1898, 303, 290; *Ber.*, 1898, 31, 890; Anschütz, *Ber.*, 1897, 30, 221; Bischoff, *Ber.*, 1897, 30, 2478, 2772; 1898, 31, 3024; Scholtz, *Ber.*, 1898, 31, 414 and 627; 1899, 32, 2251; Wedekind, *Ber.*, 1898, 31, 1746; Friedländer, *Monatsh.*, 1898, 19, 627; Paal and Schilling, *J. pr. Chem.*, 1896, [ii], 54, 277; Paal and Benker, *Ber.*, 1899, 32, 1251; Paal and Härtel, *ibid.*, 2057). The presence of ortho-alkyl groups in aromatic ketones and ketonic acids also determines very largely the behaviour of these compounds on hydrolysis (Louise, *Ann. Chim. Phys.*, [vi], 1885, 6, 206; Elbs, *J. pr. Chem.*, [ii], 1887, 35, 465; V. Meyer, *Ber.*, 1895, 28, 1270; Muhr, *ibid.*, 3215, and Weiler, *Ber.*, 1899, 32, 1908).

† Victor Meyer, in discussing the atomic volume value, suggests "dass das Estergesetz uns ein Mittel in die Hand gebe die relative Raumerfüllung der Atome in den organischen Verbindungen mit einander zu vergleichen." The varying inhibiting influence of the same element in acids and in phenols seems to preclude the acceptance of this suggestion.

manner, and that initially they give rise to keto-dihydro-derivatives (*Monatsh.*, 1895, 16, 140). According to this view,  $\beta$ -naphthol would be first converted into the compound



and on losing water this would yield  $\beta$ -ethoxynaphthalene. Evidence to a certain extent in favour of this view may be found in the behaviour of  $\beta$ -naphthol in contrast with that of phenol. Experiments made by Mr. Panisset, at Dr. Armstrong's suggestion, show that phenol and parabromophenol may be partially etherified by means of alcohol and sulphuric acid, but that they yield at most about 25 per cent. of ether. Inasmuch as benzene and its derivatives are less prone to form additive compounds than are naphthalene and its derivatives, and the former are generally less readily attacked than the latter, the fact that phenol is less readily etherified than naphthol is in accordance with the view that addition precedes substitution (compare Armstrong, *Trans.*, 1887, 51, 258; Armstrong and Rossiter, *Proc.*, 1891, 7, 89). Now if benzene is represented by Kekulé's formula, it is a matter of indifference on which side of a  $\text{CO}_2\text{H}$  group the double linking is placed, but it is not unlikely that, in bromobenzoic acid, for example, it is between the unbrominated carbon atoms, so that there is an active ethenoid linking in the immediate neighbourhood of the carboxyl. But it may well be that in  $\beta$ -naphthol no such shift can take place, and that when the linking between positions 1 and 2 is rendered comparatively inactive by the introduction of a radicle into position 1, the combining power of the compound is greatly reduced. Victor Meyer's observations on the etherification of 2-chloro- or 2-hydroxy-1-naphthoic acid and of 3-chloro- and 3-hydroxy-2-naphthoic acid are equally in accordance with this view: the former are not attacked whilst the latter are readily etherified. There can be no doubt that 1-derivatives of 2-naphthoic acid will prove equally unsusceptible.

Although the structure of the nucleus has a distinct influence, it would appear that it is rather the specific attracting power of the radicle which is eventually etherified that becomes affected and diminished by the introduction of negative radicles into the nucleus in its neighbourhood. Armstrong, indeed, has suggested this in explanation of the phenomena observed by Victor Meyer, and has pointed out (*Proc.*, 1896, 12, 42) that "the formation of a salt is presumably preceded by that of a combination of acid and 'alkaloid,' from which water is then eliminated. Just as the acid attracting

power of the  $\text{NH}_2$  radicle in aniline is affected by the introduction, say, of chlorine, so in like manner, the 'alkaloid'-attracting power of the carboxyl group may be assumed to vary as radicles are introduced in its neighbourhood in place of the hydrogen, more particularly in the case of benzenoid compounds."

Whatever the ultimate explanation of the behaviour of benzenoid acids and phenols, there can be little doubt that the phenomena of etherification must be viewed from the same standpoint as those of substitution generally, as there is complete parallelism between them. Armstrong has recently called attention (*Proc.*, 1899, 15, 176; *Chem. News*, 1899, 80, 164) to the effects produced by introducing alkyl radicles in place of the hydroxylic and aminic hydrogen in phenols and amines, and to the remarkable manner in which the formation of substitution derivatives is inhibited. It is clear, in fact, that the influence of radicles in the nucleus on etherification, and, on the other hand, of etherification on the occurrence of substitution in the nucleus is reciprocal. This is further shown to be the case by the difference in the influence exercised by radicles according to their position—a single radicle in the meta-position relatively to the carboxyl of benzoic acid exercising less influence on the rate of etherification by alcohol and hydrogen chloride than does the same radicle in the para-position and much less than it does in the ortho-position. It is impossible to overlook the parallelism which such facts present with the phenomena of substitution expressed in the well-known "ortho-para" and "meta" laws.

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### V.—*Contribution to our Knowledge of the Aconite Alkaloids. Part XV. On Japaconitine and the Alkaloids of Japanese Aconite.*

By WYNDHAM R. DUNSTAN, F.R.S., and HAROLD M. READ, Assistant Chemist in the Scientific Department of the Imperial Institute.

THE examination of the physiologically active alkaloid which exists in Japanese aconite roots has already formed the subject of several communications to this and other societies; but in view both of the conflicting statements as to its composition and relationship to aconitine and of the more recent work which has been carried out by one of us on aconitine and pseudaconitine (the crystalline, toxic alkaloids of

*Aconitum Napellus* and *A. ferox* respectively), it was thought desirable that the investigation should be extended to the alkaloids of Japanese aconite.

Japanese aconite roots seem to have come into commerce about twenty years ago; they are now imported regularly, and are regarded as more toxic than those of *A. Napellus*. An exhaustive report by Dr. A. Langgaard on "Japanese and Chinese Aconite Roots" was published in 1881 (*Arch. Pharm.*, 18, 161), and from this it appears that, although the native practitioner employs many varieties of aconite, that most frequently used and exported is "Kuza-Uzu," which has been identified by various authorities as *A. Chinense*, *A. Fischeri*, and *1. Lycoctonum* respectively.

A crystalline alkaloid was first obtained from Japanese aconite roots by Paul and Kingzett (*Pharm. J.*, 1877, [iii], 8, 173). The alkaloid was soluble in ether, insoluble in water, and formed uncrystallisable salts. From the results of a single combustion for carbon and hydrogen, and one nitrogen determination, the formula  $C_{29}H_{43}O_9N$  was adopted. This, however, was not controlled by the analysis of the platinum salt. This alkaloid was said not to suffer hydrolysis into benzoic acid and a basic substance.

In 1879, Wright, Luff, and Menke extended their investigations of the alkaloids of other aconites to those of Japanese aconite. The general results of their work (*Trans.*, 1879, 35, 387) may be briefly stated as follows:

1. The roots imported from Japan were considerably richer in active crystalline alkaloids, as well as in non-crystalline bases, than *A. Napellus*.

2. Only one crystalline alkaloid, named *japaconitine*, was present. This melted at 184—186°, and the formula  $C_{66}H_{88}O_{21}N_2$  was proposed, the base being regarded as the sesqui-apo-derivative of a parent substance having the formula  $C_{88}H_{47}O_{12}N$ .

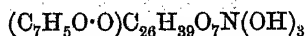
3. Japaconitine formed readily crystallisable salts, especially with nitric, hydrochloric, and hydrobromic acids. The hydrobromide has the formula  $C_{66}H_{88}O_{21}N_2 \cdot 2HBr + 5H_2O$ .

4. The alkaloid could be entirely extracted from the roots by means of alcohol alone.

5. When hydrolysed, japaconitine furnished benzoic acid and a new base, japaconine, which was amorphous, and formed amorphous salts.

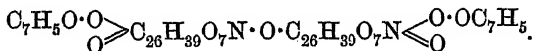
6. When either the parent base or the hydrolytic base is benzoylated, a derivative was formed containing four benzoyl groups for every  $C_{33}$  originally present.

For the hypothetical parent base, the formula





was proposed, whilst japaconitine, being the sesqui-apo-derivative, was given the formula



In 1885, K. F. Mandelin examined a specimen of japaconitine prepared by Merck, and stated that the alkaloid from Japanese roots agreed in chemical and physical behaviour with aconitine derived from *A. Napellus*.

Lübke (*Chem. Centr.*, 1890, ii, 148) arrived at the same conclusion, working with material which he extracted from "kuza-uzu" roots imported direct from Japan. The alkaloid which he isolated crystallised in rhombic prisms melting at 183—184°. It must be noted that the proof of the identity of his base with that obtained from *A. Napellus* by Wright rests on the results of a single combustion.

Still more recently, Freund and Beck (*Ber.*, 1894, 27, 723) have stated that "they have no doubt of the identity of the alkaloid from both sources," although they do not give any details of the work which led them to this conclusion.

The roots from which we have extracted the alkaloid used for this investigation were purchased in commerce as Japanese aconite roots, Mr. E. M. Holmes, F.L.S., Curator of the Pharmaceutical Society's Museum, kindly examined a specimen of these, and informed us that they are undoubtedly ordinary Japanese roots, such as described by Langgaard (*loc. cit.*, and *Pharm. J.*, 1881, [iii], 11, 1043), and known in Japan as "kuza-uzu."

## I. JAPACONITINE.

### *Extraction of the Alkaloid.*

We have extracted the alkaloid by the following method. The finely ground root is percolated with a mixture of amyl alcohol and wood spirit, in the proportion of 1 part of the former to 5 of the latter. The complete exhaustion takes a considerable time.

The wood spirit is distilled from the mixture under reduced pressure on a water-bath, the temperature of which is kept below 60°; the residual solution of the alkaloids in amyl alcohol is extracted with dilute (0.5 per cent.) sulphuric acid, and the latter thoroughly washed with ether to remove all traces of amyl alcohol. The alkaloid is now fractionally precipitated by sodium carbonate or ammonia from the aqueous solution of the sulphate, and is extracted by shaking with ether. When the whole of the bases soluble in ether have been removed, the extraction is continued with chloroform.

The aqueous mother liquors still contain a small quantity of alkaloid,

a certain proportion of which may be removed by saturating the solution with sodium sulphate and then shaking with chloroform.

The ethereal solution is now washed with water to remove traces of alkali, and calcium chloride is added. The latter serves a double purpose in precipitating most of the colouring matter extracted by the ether, and at the same time drying the solution. Since the calcium chloride does not show any tendency to combine with the alkaloid, this method is very advantageous in avoiding a great deal of subsequent purification. The dried and filtered solution is carefully distilled, and, when sufficiently concentrated, the nearly pure japaconitine crystallises out in minute, colourless rosettes of prismatic needles. From the mother liquor, a further quantity of crystalline japaconitine may be obtained. The best method for working up the solution in chloroform is to wash it with water to remove traces of alkali, evaporate to a small volume, drive off the residual chloroform with a current of air, and then to add ether to the pale brown varnish which remains. The greater part of the varnish dissolves in the ether, and on pouring off and evaporating the latter solution, more crystalline japaconitine is obtained. The extract left undissolved by the ether will be described later (see page 62).

#### *Properties of Japaconitine.*

The crystalline base obtained in this manner melts at about 195–196°. For the final purification, it is converted into a salt, preferably the hydrobromide, by dissolving in the diluted acid and evaporating the neutral solution in a vacuum desiccator until crystals form. The crystallisation may be considerably hastened by well stirring the solution with a glass rod. We have found that, in evaporating the solution, it is well to avoid entirely the aid of heat, since the saving of time effected is more than counterbalanced by the discoloration of the resulting salt. Having recrystallised the salt, either from water or from a mixture of alcohol and ether, until the melting point remains unchanged, the base may be regenerated in the usual manner.

When thus purified, japaconitine crystallises from ether, alcohol, or chloroform in colourless, anhydrous rosettes of needles. The base recrystallised from ether was analysed.

0.5518	lost 0.002	after 30 minutes	at 100°.	Loss = 0.362	per cent
0.6267	„ 0.0003	„ 90	„ 100°.	Loss = 0.047	„

The base therefore does not combine with the solvent.

Many attempts were made to obtain large crystals for crystallographic measurement, but these, unfortunately, have been unsuccessful.

This difficulty in obtaining large crystals of japaconitine contrasts

sharply with the ease with which, by the same methods, the well-defined, hexagonal prisms so characteristic of aconitine are obtained. The largest japaconitine crystals we have succeeded in preparing were obtained by the gradual precipitation of a solution in dry chloroform with light petroleum. These were kindly examined for us by Mr. W. J. Pope, who describes them as follows :

"The crystals of japaconitine are very small, transparent, colourless needles possessing a brilliant lustre ; the sides of the needles are made up of two pairs of parallel prism faces. A number of measurements of the prism angle showed this to have the value  $77^{\circ} 35'$ — $77^{\circ} 54'$  ; no measurements in which the end faces of the needles were involved could be made owing to the minute size of these end faces.

"The extinction in the prism faces is straight, and on examination in convergent light the interference figure of a uniaxial substance, or of a biaxial substance with a very small optic axial angle, is seen emerging in the angle between the prism faces ; the double refraction is negative in sign. On examining the crushed crystals microscopically, pieces may sometimes be found in which the optic axial interference figure occupies the centre of the field ; some pieces show a uniaxial figure, whilst in others the interference figure is biaxial with a very small optic axial angle.

"On comparing the above description with that of aconitine given by Tutton (Trans., 1891, 59, 288) or of pseudaconitine by Pope (Trans., 1897, 71, 352), no points of similarity are traceable ; it must therefore be concluded that japaconitine is crystallographically different from both aconitine and pseudaconitine."

Japaconitine is very soluble in acetone, wet alcohol, and chloroform, and, when amorphous, in dry alcohol and in ether. When crystalline, it slowly dissolves in boiling ether and alcohol. It is almost insoluble in dry light petroleum, and is but slightly soluble in water. It is readily crystallised by the addition either of water to its solution in alcohol or in acetone, or of petroleum to its solution in chloroform, or in alcohol and ether.

The pure base melts at  $204.5^{\circ}$  (corr.) to a clear, pale yellow liquid, which, a few seconds later, effervesces rapidly with the evolution of acetic acid.

#### *Specific Rotation of Japaconitine*

Lübbe (*loc. cit.*) has stated that a 3 per cent. alcoholic solution of japaconitine is inactive. We find, on the contrary, that both alcoholic and chloroform solutions are dextrorotatory, like those of aconitine (Dunstan and Ince, Trans., 1891, 59, 281).

- (1) In chloroform.  $[\alpha]_D = +20.26^\circ$  (mean).  
 $\alpha^{19^\circ} = +0.622^\circ$ ;  $l = 2$  dm.;  $c = 1.602$ ;  $[\alpha]_D^{19^\circ} = +19.41^\circ$ .  
 $\alpha^{15^\circ} = +0.6^\circ$ ;  $l = 2$  dm.;  $c = 1.42$ ;  $[\alpha]_D^{15^\circ} = +21.12^\circ$ .
- (2) In alcohol.  $[\alpha]_D = +23.6^\circ$ .  
 $\alpha^{18.5^\circ} = +17.2'$ ;  $l = 2$  dm.;  $c = 0.605$ ;  $[\alpha]_D^{18.5^\circ} = +23.6^\circ$ .

The specific rotatory power of japaconitine is therefore much greater than that of aconitine, which is only  $+11^\circ$  in alcohol (Dunstan and Ince, *loc. cit.*), whilst in chloroform we find it to be  $+14.61^\circ$  at  $18^\circ$ .

#### *Determination of Methoxyl Groups in Japaconitine.*

The number of methoxyl groups in the base was estimated in the usual manner, using a slight modification of Zeisel's method.

0.1806 gave 0.268 AgI.  $\text{CH}_3\text{O} = 19.58$ .

0.1852 „ 0.279 AgI.  $\text{CH}_3\text{O} = 19.87$ .

$\text{C}_{30}\text{H}_{37}\text{O}_7\text{N}(\text{OCH}_3)_4$  requires  $\text{CH}_3\text{O} = 19.16$  per cent.

Japaconitine therefore, like aconitine, contains four methoxyl groups.

#### *Combustions of Japaconitine.*

The pure base was burnt in a current of oxygen, using cupric oxide and a silver spiral.

0.2857 gave 0.6534  $\text{CO}_2$  and 0.2005  $\text{H}_2\text{O}$ .  $\text{C} = 62.37$ ;  $\text{H} = 7.79$ .

0.2814 „ 0.6410  $\text{CO}_2$  „ 0.1790  $\text{H}_2\text{O}$ .  $\text{C} = 62.12$ ;  $\text{H} = 7.06$ .

0.1888 „ 0.4338  $\text{CO}_2$  „ 0.1198  $\text{H}_2\text{O}$ .  $\text{C} = 62.66$ ;  $\text{H} = 7.05$ .

0.2049 „ 0.4740  $\text{CO}_2$  „ 0.1322  $\text{H}_2\text{O}$ .  $\text{C} = 63.09$ ;  $\text{H} = 7.16$ .

Mean,  $\text{C} = 62.56$ ;  $\text{H} = 7.26$  per cent.

Two combustions for nitrogen by the absolute method, using lead chromate, furnished the following data:

0.3035 gave 8.892 mg. moist nitrogen.  $\text{N} = 2.92$ .

0.3105 „ 7.864 mg. moist nitrogen.  $\text{N} = 2.53$ .

$\text{C}_{34}\text{H}_{49}\text{O}_{11}\text{N}$  requires  $\text{C} = 63.06$ ;  $\text{H} = 7.57$ ;  $\text{N} = 2.16$  per cent.

We therefore adopt this formula provisionally as best representing the composition of japaconitine. This formula differs only very slightly from that proposed for aconitine by Freund and Beck (*Ber.*, 1894, 27, 433).

#### *Salts of Japaconitine.*

Japaconitine, like aconitine, furnishes a number of well crystallised salts.

*Japaconitine hydrochloride* is readily obtained by dissolving the pure base in dilute hydrochloric acid, the solution being left faintly acid

to litmus. The salt crystallises out in plates melting at 149—150°. When crystallised by dissolving in alcohol and precipitating with ether, lustrous rosettes of hexagonal plates, melting at 149—150°, are obtained. The salt crystallised from aqueous alcohol and ether contains three molecular proportions of water.

0.7800 lost 0.0640 after  $1\frac{1}{2}$  hours at 105—110°. Loss = 8.2.

0.3230 gave 0.0604 AgCl. Cl = 4.62.

$C_{34}H_{49}O_{11}N \cdot HCl + 3H_2O$  requires Cl = 4.81;  $H_2O = 7.3$  per cent.

It has already been shown (Dunstan and Ince, *loc. cit.*, Dunstan and Carr, Trans., 1897, 71, 350) that although aconitine and pseudaconitine are dextrorotatory, their salts are levorotatory. Japaconitine also exhibits this peculiarity.

The tri-hydrated salt dissolved in water was used for the following determination :

$$\alpha_D^{17} = -1.466^\circ; l = 2 \text{ dm.}; c = 3.076; [\alpha]_D^{17} = -23.8^\circ.$$

A determination of the specific rotation of aconitine hydrochloride was made at the same temperature for comparison :

$$\alpha_D^{17} = -1.433^\circ; l = 2 \text{ dm.}; c = 2.315; [\alpha]_D^{17} = -30.9^\circ.$$

*Japaconitine hydrobromide* crystallises readily from water, or from alcohol and ether. The crystals deposited from the latter solvents are very similar to those of the hydrochloride, being rosettes of hexagonal plates. When dried, the salt melts at 172—173°.

The salt crystallised from aqueous alcohol and ether contains four molecular proportions of water.

1.2860 lost 0.1044 after 2 hours at 105—110°. Loss = 8.11.

0.3320 „ 0.0278 „ „ 100—110°. Loss = 8.37.

0.3060 gave 0.0726 AgBr. Br = 10.09.

$C_{34}H_{49}O_{11}N \cdot HBr + 4H_2O$  requires Br = 10.00;  $H_2O = 9.00$  per cent.

*Japaconitine hydriodide* crystallises from water in minute rosettes melting at 195—197°. When recrystallised from alcohol and ether, the salt melts at 207.5—208.5°.

*Japaconitine nitrate* crystallises from water in minute rosettes of needles melting at 173—177°.

When recrystallised from alcohol and ether, the salt contains one molecular proportion of water and melts at 194°, effervescing sharply at 199°. The water of crystallisation is not lost until the salt is heated to 115—120°. After being dried at 100°,

0.5315 lost 0.01 at 115—120° for  $1\frac{1}{2}$  hours. Loss = 1.9 per cent.

The hydrated salt gave the following numbers on analysis:

0.1762 gave 0.3620  $\text{CO}_2$  and 0.1145  $\text{H}_2\text{O}$ .  $\text{C}=56.03$ ;  $\text{H}=7.22$ .  
 $\text{C}_{34}\text{H}_{49}\text{O}_{11}\text{N}, \text{HNO}_3 + \text{H}_2\text{O}$  requires  $\text{C}=56.04$ ;  $\text{H}=7.14$ ;  $\text{H}_2\text{O}=2.47$   
per cent.

*Japaconitine thiocyanate* is prepared by adding an aqueous solution of ammonium thiocyanate to an aqueous solution of japaconitine hydrochloride. The crystalline salt, melting at  $120^\circ$ , is immediately precipitated if the alkaloidal solution is strong. When dissolved in alcohol and precipitated with water, the salt crystallises in lustrous needles. These melt at  $190$ – $192^\circ$ . *Aconitine thiocyanate*, crystallised from water, melts at  $145^\circ$ ; crystallised from alcohol and ether, it melts at  $193$ – $195^\circ$ .

*Japaconitine aurichloride* is obtained as a bulky, amorphous, canary-yellow precipitate by the addition of an aqueous solution of auric chloride to an aqueous solution of japaconitine hydrochloride slightly acidified with hydrochloric acid. The precipitate is quickly filtered, washed with water until the washings are neutral, and then dried in a vacuum. The amorphous aurichloride is readily soluble in alcohol, chloroform, or acetone, slightly soluble in water. A few minutes after the amorphous salt is dissolved in a little alcohol, the greater part of it separates in minute, golden-yellow, opaque needles which melt at  $231^\circ$  (uncorr.). The same salt may be prepared by precipitating (1) methyl or ethyl alcohol, or acetone solutions with ether or with water, (2) chloroform solutions with ether or with ether and petroleum. In each case, crystalline japaconitine aurichloride, melting at  $231^\circ$ , is obtained.

On two occasions we have obtained yellow crystals of an aurichloride melting at a much lower temperature. First, by dissolving the amorphous salt in dry chloroform and allowing the solvent to evaporate spontaneously, yellow prisms separated. These melted indistinctly at  $152$ – $154^\circ$ . They were recrystallised by dissolving in chloroform and precipitating with ether, when similar prisms melting at  $153^\circ$  were obtained. On attempting to recrystallise these from alcohol, it was found that they separated from that solvent almost immediately after solution, in the opaque, small, canary-yellow rosettes which we find to be so characteristic of japaconitine aurichloride. These rosettes melted at  $231^\circ$ .

On the second occasion, a crystalline, golden-yellow aurichloride, melting indistinctly at  $154$ – $160^\circ$ , was obtained after the addition of dry, light petroleum to an alcoholic solution of the amorphous salt. These crystals dissolved in chloroform, and on the addition of ether were precipitated in opaque rosettes melting at  $231^\circ$ . They were therefore japaconitine aurichloride.

One of us has already shown (Dunstan and Jowett, Trans., 1893,

63, 994) that aconitine aurichloride may exist in three distinct isomeric forms, the nature of the solvent and of the precipitant being apparently the factors which determine the production of these modifications. Although we have been unable to find the exact conditions for the formation of the salt of japaconitine melting at  $154-156^{\circ}$ , it is evident from these results that japaconitine aurichloride exists in at least two isomeric forms. The stable modification melting at  $231^{\circ}$ , being that most generally produced, we propose to name *japaconitine  $\alpha$ -aurichloride*, and the unstable variety, melting indistinctly at  $154-160^{\circ}$ , *japaconitine  $\beta$ -aurichloride*. The melting points of aconitine  $\alpha$ -,  $\beta$ -,  $\gamma$ -aurichlorides are  $135.5^{\circ}$ ,  $151-152^{\circ}$ , and  $176^{\circ}$  respectively.

In this connection, it is of interest to note that japaconitine and aconitine, when mixed, may, by a tedious process, be separated by repeatedly fractionating the aurichlorides of the mixed bases by crystallisation from alcohol and from a mixture of alcohol and ether. Japaconitine  $\alpha$ -aurichloride, melting at  $231^{\circ}$ , crystallises out in the first fractions, and aconitine  $\beta$ -aurichloride, melting at  $151-152^{\circ}$  in the later fractions.

Japaconitine  $\alpha$ -aurichloride forms neither a hydrate nor an alcoholate. The crystalline salt, after being dried on a porous tile, lost no weight, either when allowed to remain in a vacuous desiccator for several days, or when heated in the water oven.

A determination of the gold and chlorine gave the following results :

0.2408 gave 0.0474 Au and required 9.8 c.c. of  $N/10$   $\text{AgNO}_3$  (of which 983 c.c. = 3.55 Cl) for complete precipitation of the chlorine. Whence  $\text{Au} = 19.68$  ;  $\text{Cl} = 14.69$  per cent.

The salt was burnt for carbon and hydrogen, but the determination of the latter was of no value.

0.2014 gave 0.3010  $\text{CO}_2$ .  $\text{C} = 40.76$  per cent.

$\text{C}_{34}\text{H}_{49}\text{O}_{11}\text{N}, \text{HAuCl}_4$  requires  $\text{Au} = 19.95$  ;  $\text{Cl} = 14.38$  ;  $\text{C} = 41.33$  per cent.

#### *Physiological Action of Japaconitine.*

The physiological action of japaconitine is being investigated by Professor Cash. It may be stated here that it is an intensely toxic alkaloid which, in general, acts like aconitine, the resemblance between the two alkaloids being very close indeed.

It produces the characteristic tingling of the lips, tongue, and skin, with long-continued tactile and thermic perception at the seat of application. It slows and then accelerates the heart, producing a sequence of ventricular upon auricular action. The death occasioned by it appears, however, to be primarily respiratory. Whilst the lethal

dose of japaconitine towards frogs (*Rana esculenta* and *R. temporaria*) and mammals is not identical with that of aconitine, the difference in toxicity is not great, moreover the variation in the effect produced by an equal dose is one rather of degree than of kind.

*Action of Methyl Iodide on Japaconitine. Methyljapaconitine.*

When japaconitine is heated in a closed tube to a temperature of 110—112° with a slight excess of methyl iodide, a crystalline methiodide is formed. This methiodide crystallises from the mother liquor with extreme readiness in large rosettes of colourless needles which melt at 224—225°.

0.2240 dissolved in alcohol and precipitated with silver nitrate, furnished 0.0690 AgI. I = 16.64.

$C_{34}H_{49}O_{11}N, CH_3I$  requires I = 16.09 per cent.

On adding dilute potash to an aqueous solution of japaconitine methiodide, a flocculent precipitate of *methyljapaconitine*,  $C_{34}H_{48}O_{11}N \cdot OH$ , is thrown down. This base may be readily extracted by chloroform or ether, and crystallises from the latter in minute rosettes of colourless needles, which melt at 206°.

A combustion of the pure base furnished the following data:

0.1142 gave 0.2670  $CO_2$  and 0.0790  $H_2O$ . C = 63.76; H = 7.69.

$C_{35}H_{51}O_{11}N$  requires C = 63.54; H = 7.71 per cent.

*Methyljapaconitine aurichloride* crystallises from a mixture of alcohol and ether in minute rosettes which melt at 223—225°.

The readiness with which japaconitine furnishes a methyl derivative is another point of difference between it and aconitine (Dunstan and Jowett, Proc., 1894, 10, 96).

*Action of Acetyl Chloride on Japaconitine. Triacetyljapaconitine.*

By allowing acetyl chloride to act on japaconitine for some hours a triacetyl derivative melting at 166° is formed. In addition to this, a small quantity of a derivative very soluble in alcohol, and melting at 184—186°, is produced, but the amount obtained was too small for further examination.

*Triacetyljapaconitine*,  $C_{34}H_{46}O_{11}N(CO \cdot CH_3)_3$ , crystallises in colourless rosettes melting at about 166°. It is not very soluble in alcohol, and may thus be easily separated from the derivative melting at 184—186°. It is soluble in ether and in chloroform, but insoluble in water.

0.1043 gave 0.2357  $CO_2$  and 0.0697  $H_2O$ . C = 61.63; H = 7.41.

0.2475 „ on hydrolysis with potash, 29.5 per cent. acetic acid.

$C_{40}H_{55}O_{14}N$ , requires C = 62.09; H = 7.11;  $C_2H_4O_2$  = 31.04 per cent.



## II. JAPBENZAONINE.

*Hydrolysis of Japaconitine.*

When japaconitine is hydrolysed, it furnishes acetic acid, and a new crystalline base, which from its analogy to benzaconine, the hydrolytic base from aconitine, we purpose naming *japbenzaconine*. This hydrolysis may be effected in neutral, in alkaline, or in slightly acid solution. The last is the most convenient, since in the presence of alkalis, the new base, japbenzaconine, readily suffers further hydrolysis into benzoic acid, and another base, japaconine (*vide infra*). Although any of the salts of japaconitine may be used for the hydrolysis, we have found the sulphate to give the most satisfactory results. 0.4122 gram of japaconitine was neutralised with dilute sulphuric acid and the solution heated in a sealed tube for 9 hours at 115–130°. The slightly discoloured solution was then neutralised with soda. A definite amount of decinormal sulphuric acid was now added and the benzoic acid, a small quantity of which is invariably produced, removed by shaking with benzene. The aqueous portion and the washings from the benzene were titrated with soda (1020 c.c. = 4.9 H<sub>2</sub>SO<sub>4</sub>) of which 6.6 c.c. were required, equivalent to 9.41 per cent. acetic acid. The equation  $C_{34}H_{49}O_{11}N + H_2O = C_2H_4O_2 + C_{32}H_{47}O_{10}N$  requires 9.27 per cent. The identity of the acid was proved by an analysis of its silver salt.

0.1485 gave 0.0957 Ag. Ag = 64.44.

C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>Ag requires Ag = 64.66 per cent.

The identity of the benzoic acid, extracted by benzene, was determined by its melting point, which was 121°, as well as by other of its physical characters (*vide infra*). No methyl alcohol or other product could be detected. The hydrolysis, therefore, takes place according to the equation given above.

Wright and Luff do not record the production of acetic acid during the hydrolysis of japaconitine, nor did they observe the formation of japbenzaconine. Their account of the hydrolysis is that the japaconitine is decomposed, forming japaconine and benzoic acid.

*Properties of Japbenzaconine.*

The new base is precipitated from the aqueous solution of its salts by the addition of alkali, and may be partially removed by shaking with ether. Its complete removal necessitates a vigorous shaking with chloroform. By the evaporation of its ethereal solution, japbenzaconine is obtained as a colourless varnish. The latter readily

dissolves in dilute hydrochloric acid, the solution, after partial evaporation and stirring, yielding a crystalline salt. Although no difficulty attends the crystallisation of the salts of japbenzaconine, many attempts were made to crystallise the base before it was accomplished. The following method finally proved successful. A slight excess of dilute ammonia was added to an aqueous solution of the pure hydrochloride, the white flocks of the precipitated base dissolved by shaking with ether, and the ethereal solution washed and dried over calcium chloride. The dried solution was filtered into a stoppered bottle, and sufficient light petroleum added to produce a faint opalescence. A considerable quantity of amorphous japbenzaconine separated, and after standing 2 or 3 days the clear mother liquor was poured off into another bottle. After several days, minute rosettes appeared. These melted at  $176^{\circ}$ ; further small quantities of crystals having the same melting point were obtained by the careful addition to the mother liquor of small quantities of light petroleum. When purified by recrystallisation from a mixture of ether and petroleum, the base melted at  $183^{\circ}$ . It could also be crystallised by dissolving in alcohol and precipitating with water. The crystals thus obtained melted at about  $180^{\circ}$ .

Japbenzaconine, therefore, differs very markedly from benzaconine in the fact that it may, when pure, be fairly readily crystallised. The only well-defined crystals we have obtained were rhombohedral plates. When dissolved in dilute acids, the solution is distinctly bitter, and quite free from the tingling sensation so characteristic of japaconitine and of aconitine. The base, crystallised from ether, is anhydrous.

0.1967 lost 0.003 after 1 hour at  $103^{\circ}$ , that is, 1.53 per cent.

*Specific rotation of japbenzaconine.* In alcohol.

$$\alpha_{D}^{18.5} = +1.633^{\circ}; l = 2 \text{ dcm.}; c = 2.033; [\alpha]_D^{18.5} = +40.16^{\circ}.$$

The specific rotation of benzaconine is  $+4.48$  (Dunstan and Harrison, *Trans.*, 1893, **63**, 443). Japbenzaconine is therefore nearly ten times more optically active than benzaconine.

Combustions of japbenzaconine:

0.1922 gave 0.4510  $\text{CO}_2$  and 0.1505  $\text{H}_2\text{O}$ . C = 63.99; H = 8.7.

0.1857 „ 0.4365  $\text{CO}_2$  „ 0.1252  $\text{H}_2\text{O}$ . C = 64.10; H = 7.49.

$\text{C}_{32}\text{H}_{47}\text{O}_{10}\text{N}$  requires C = 63.47; H = 7.76.

#### *Salts of Japbenzaconine.*

The salts of japbenzaconine crystallise with extreme readiness.

*Japbenzaconine hydrochloride* crystallises from water in minute rosettes melting at  $244\text{--}245^{\circ}$ . When recrystallised from alcohol and

ether, the melting point is raised to  $253^{\circ}$ . The salt, crystallised from alcohol and ether, contains one molecular proportion of water.

0.2234 hydrated salt lost 0.0044  $\text{H}_2\text{O}$  after  $1\frac{1}{2}$  hours at  $100^{\circ}$ .  
 $\text{H}_2\text{O} = 1.97$ .

0.2009 hydrated salt lost 0.0057  $\text{H}_2\text{O}$  after heating  $\frac{1}{2}$  hour at  $110^{\circ}$ .  
 $\text{H}_2\text{O} = 2.33$ .

0.1950 hydrated salt gave 0.0416  $\text{AgCl}$ .  $\text{Cl} = 5.27$ .

0.2066 „ „ 0.0446  $\text{AgCl}$ .  $\text{Cl} = 5.34$ .

$\text{C}_{32}\text{H}_{47}\text{O}_{10}\text{N}, \text{HCl} + \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 2.73$ ;  $\text{Cl} = 5.38$  per cent.

Specific rotation of the hydrated hydrochloride in water.

$$\alpha^{23^{\circ}} = -0.8^{\circ}; l = 2 \text{ dcm.}; c = 2.028; [\alpha]_D^{23^{\circ}} = -19.73^{\circ}.$$

The specific rotation of benzaconine hydrochloride, dissolved in water, was taken for comparison.

$$\alpha^{23^{\circ}} = 0.75^{\circ}; l = 2 \text{ dcm.}; c = 1.492; [\alpha]_D^{23^{\circ}} = -25.13^{\circ}.$$

Combustions of the anhydrous hydrochloride.

0.1894 gave 0.4175  $\text{CO}_2$  and 0.1240  $\text{H}_2\text{O}$ .  $\text{C} = 60.11$ ;  $\text{H} = 7.27$

0.1925 „ 0.4242  $\text{CO}_2$  „ 0.1281  $\text{H}_2\text{O}$ .  $\text{C} = 60.09$ ;  $\text{H} = 7.39$ .

$\text{C}_{32}\text{H}_{47}\text{O}_{10}\text{N}, \text{HCl}$  requires  $\text{C} = 59.95$ ;  $\text{H} = 7.49$  per cent.

*Japbenzaconine hydrobromide* crystallises from water in minute prisms, and from alcohol and ether in rosettes melting indistinctly about  $205\text{--}217^{\circ}$ .

*Japbenzaconine aurichloride* is precipitated in amorphous, yellow flocks on mixing aqueous solutions of auric chloride and of japbenzaconine hydrochloride. The dried amorphous salt crystallises immediately upon the addition of dry alcohol, the crystals melting at about  $212^{\circ}$ . The salt may be readily crystallised from alcohol or chloroform by precipitation with ether. The melting point varies with the nature of the solvent, the crystals from alcohol melting at  $219^{\circ}$ , and those from chloroform and ether at  $228^{\circ}$ . By the addition of water to an alcoholic solution, the salt is precipitated in oily drops. The crystalline aurichloride is anhydrous.

Analysis of the salt furnished the following results.

0.3320 gave 0.0675  $\text{Au}$  and 0.189  $\text{AgCl}$ .  $\text{Au} = 20.33$ ;  $\text{Cl} = 14.08$ .

$\text{C}_{32}\text{H}_{47}\text{O}_{10}\text{N}, \text{HAuCl}_4$  requires  $\text{Au} = 20.84$ ;  $\text{Cl} = 15.02$  per cent.

The hydrochloride of the regenerated base crystallised readily from water, melted at  $246^{\circ}$ , and was identical with japbenzaconine hydrochloride.

*Aurichlor-japbenzaconine*.—When an alcoholic solution of japbenzaconine aurichloride, to which a few drops of light petroleum

have been added, is allowed to stand for about a week, colourless, well-defined, lustrous octahedra are obtained. These octahedra, after recrystallisation from alcohol and ether, melt at  $178^{\circ}$  with the separation of a considerable quantity of gold. The mother liquor from which these crystals separated furnished a small quantity of colourless rosettes of needles melting at about  $230^{\circ}$  and containing gold. The quantity obtained was unfortunately too small for further examination. The octahedra, melting at  $178^{\circ}$ , crystallise without any attached solvent. An analysis furnished the following data:

0.2332 gave 0.053 Au and 0.078 AgCl. Au = 22.72; Cl = 8.27  
 $C_{32}H_{46}O_{10}N \cdot AuCl_2$  requires Au = 22.6; Cl = 8.23 per cent.

The hydrochloride of the regenerated base crystallised from alcohol and ether in beautiful, lustrous rosettes melting at  $252-253^{\circ}$ , and identical with japbenzaconine hydrochloride.

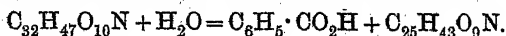
### III. JAPACONINE.

#### *Hydrolysis of Japbenzaconine.*

Japbenzaconine is slowly hydrolysed by strong alkalis or by cold dilute sulphuric acid, more rapidly on heating. The complete hydrolysis is, however, by no means easy to effect, since the continued heating with alkalis leads to the resinification of the hydrolytic products. This is obviated to a certain extent by carrying out the hydrolysis either in alcoholic solution, using an alcoholic solution of sodium hydroxide, or in a sealed tube. The former method was the one which we found most satisfactory, and gave fairly concordant results when the percentage of benzoic acid was determined.

2.9015 grams of japbenzaconine were dissolved in alcohol, warmed, and a 30 per cent. alcoholic solution of sodium hydroxide added. The mixture was allowed to stand for 24 hours. Dilution with water produced no precipitation of japbenzaconine, showing that the hydrolysis was complete. The solution was neutralised with sulphuric acid, the alcohol removed by evaporation on a water-bath, and the aqueous solution, after acidifying with sulphuric acid, extracted with benzene. The benzene solution was extracted with dilute soda, and the latter acidified with sulphuric acid and extracted with ether. The dried ethereal solution furnished, after careful evaporation, 0.589 gram of benzoic acid (m. p.  $121.5^{\circ}$ ) = 19.98 per cent.

The following equation therefore represents the hydrolysis, the calculated quantity of benzoic acid being 20.16 per cent.



The acid solution from which the benzoic acid had been removed

was now rendered alkaline, and extracted, first with ether and then with chloroform. The ether removed nothing from the solution, and the chloroform only a trace of alkaloid which was readily extracted again by shaking with water. The residual solution was therefore neutralised with sulphuric acid, and evaporated to dryness. The residue, most of which was sodium sulphate, was extracted with alcohol, the alcoholic solution made alkaline with sodium hydroxide, evaporated to dryness, and the brown alkaloidal residue dissolved in chloroform; the chloroform solution gave, after evaporation, a very hygroscopic, dark brown varnish. This varnish, which was strongly alkaline to litmus and readily reduced Fehling's solution, was purified by neutralising with aqueous sulphuric acid and removing the greater part of the colouring matter by boiling the solution with charcoal. The pure base, japaconine, was obtained by precipitating the solution of the sulphate with barium hydroxide, filtering, and evaporating the aqueous solution. It was finally purified by the fractional precipitation of a solution in chloroform with ether. Most of the colouring matter is precipitated in the first fractions, the later fractions being almost colourless japaconine.

*Properties and Composition of Japaconine.*

Thus purified, japaconine is a colourless, exceedingly hygroscopic, powder which we have so far been unable to crystallise. It is readily soluble in water, alcohol, chloroform and acetone, but almost insoluble in ether and petroleum. It melts indefinitely between 97° and 100°. Its specific rotation in water is +10.88°.

$$\alpha^{19} = +0.4^{\circ}; l=2 \text{ cm.}; c=1.837; [\alpha]_{\text{D}}^{19} = +10.88^{\circ}.$$

Combustions of the amorphous japaconine.

0.2010 gave 0.4480 CO<sub>2</sub> and 0.1460 H<sub>2</sub>O. C=60.78; H=8.07.

0.1855 „ 0.4058 CO<sub>2</sub> „ 0.1193 H<sub>2</sub>O. C=59.65; H=7.14.

0.1634 „ 0.3645 CO<sub>2</sub> „ 0.1108 H<sub>2</sub>O. C=60.77; H=7.53.

C<sub>25</sub>H<sub>48</sub>O<sub>9</sub>N requires C=59.88; H=8.58 per cent.

The salts of japaconine crystallise with great difficulty. None crystallise from water, and those which we have crystallised from alcohol and ether are so hygroscopic that we have, unfortunately, been unable to examine them completely.

*Japaconine hydrobromide* crystallises from alcohol and ether in rosettes of colourless, triangular plates melting sharply at 221°.

*Japaconine hydrochloride* crystallises from alcoholic solution after the addition of ether.

*Japaconine oxalate* crystallises in colourless, dumb-bell shaped rosettes.

A strong aqueous solution of the hydrochloride gives no precipitate with auric chloride or platinic chloride, and the aqueous solution of the aurichloride is quickly reduced. Fehling's solution is also reduced when boiled with a solution of japaconine.

In its general behaviour, japaconine resembles aconine; its salts, however, crystallise much less readily than those of aconine.

#### IV. PYROJAPACONITINE.

##### *Effect of Heat on Japaconitine.*

It has already been shown (Dunstan and Carr, Trans., 1894, 65, 176; 1897, 71, 350) that aconitine and pseudaconitine decompose when heated at their melting points, furnishing acetic acid and new bases which were named pyraconitine and pyropseudaconitine respectively. We find that japaconitine behaves in a similar manner. When heated at about 200—210° for 10 minutes, the base gradually darkens, and finally melts, with the evolution of acetic acid. The amount of the latter, estimated by titration with decinormal soda solution, varies from 8.4 to 8.9 per cent. The amount required for a loss of one molecule of acid from one molecule of japaconitine ( $C_{84}H_{49}O_{11}N - C_2H_4O_2$ ) = 9.27 per cent. In addition to the loss of the acetic acid, there is almost invariably a further loss varying from 3 to 4.5 per cent., the nature of which has not been determined.

The dark brown varnish which remained after the evolution of the acetic acid was readily purified by dissolving in dilute sulphuric acid, exactly neutralising the solution with soda, and boiling with charcoal for a few minutes. Ammonia was added to the colourless solution thus obtained, and the bulky, flocculent precipitate of the pyro-base extracted by shaking several times with ether and finally with chloroform. The ethereal solution was dried with calcium chloride and evaporated to dryness, a pale yellow varnish being thus obtained. This varnish was dissolved in dilute hydrobromic acid, and the solution evaporated to a small bulk on a water-bath. After vigorous stirring, minute crystals of the salt separated, which melted at 240° (pyraconitine hydrobromide melts at 282°). The base was regenerated and extracted with ether, and the ethereal solution, after partial evaporation, dried with calcium chloride, filtered into a stoppered bottle, and light petroleum added until an opalescence formed. Colourless needles of the base crystallised after standing a few days. These, after crystallisation, melted at 167—168°.

The alkaloid, like pyraconitine, is laevorotatory.

$$\alpha^{20} = -3.33^\circ; l = 2 \text{ dm.}; c = 2.529; [\alpha]_D^{20} = -65.89.$$

On combustion, the crystalline base furnished the following results :

0.1081 gave 0.2582  $\text{CO}_2$  and 0.0685  $\text{H}_2\text{O}$ .  $\text{C} = 65.14$ ;  $\text{H} = 7.04$ .

0.1079 „ 0.2572  $\text{CO}_2$  „ 0.0652  $\text{H}_2\text{O}$ .  $\text{C} = 64.92$ ;  $\text{H} = 6.71$ .

$\text{C}_{32}\text{H}_{45}\text{O}_9\text{N}$  requires  $\text{C} = 65.41$ ;  $\text{H} = 7.66$  per cent.

A methoxyl determination by Zeisel's method shows that pyrojapaconitine, like japaconitine, contains four methoxyl groups.

0.1950 furnished 0.2810  $\text{AgI}$ .  $\text{CH}_3\text{O} = 19.00$ .

$\text{C}_{32}\text{H}_{45}\text{O}_9\text{N}$  requires, for 3 methoxyl groups,  $\text{CH}_3\text{O} = 15.8$  per cent.

„ „ 4 „ „  $\text{CH}_3\text{O} = 21.1$  „

Pyrojapaconitine furnishes well crystallised salts.

*Pyrojapaconitine hydrobromide* separates from water in minute, colourless crystals melting at  $241^\circ$ . When this salt is recrystallised by dissolving in alcohol and precipitating with ether, it melts at  $208$ — $209^\circ$ , but, after solidification, it remelts at about  $237$ — $238^\circ$ . The melting point of this ( $208^\circ$ ) variety is unchanged by repeated recrystallisation from dry alcohol and ether, but when recrystallised from water the salt melts at  $241^\circ$ .

The salt, crystallised from its aqueous solution, contains two molecular proportions of water, one only of which is lost at  $100^\circ$ .

0.7140 lost 0.0293  $\text{H}_2\text{O}$  after 2 hours at  $100^\circ$ .  $\text{H}_2\text{O} = 4.10$ .

0.4415 „ 0.0180  $\text{H}_2\text{O}$  „ 70 minutes at  $100$ — $130^\circ$ .  $\text{H}_2\text{O} = 4.8$ .

The specific rotation of pyrojapaconitine hydrobromide in water is  $-102.5^\circ$ .

$$\alpha_{\text{D}}^{25} = -5.616^\circ; l = 2 \text{ dm.}; c = 2.7388; [\alpha]_{\text{D}}^{25} = -102.5^\circ.$$

On analysis, the salt, dried at  $100^\circ$ , furnished the following data :

0.1815 gave 0.3706  $\text{CO}_2$  and 0.1030  $\text{H}_2\text{O}$ .  $\text{C} = 55.68$ ;  $\text{H} = 6.30$ .

0.1910 „ 0.3910  $\text{CO}_2$  „ 0.1110  $\text{H}_2\text{O}$ .  $\text{C} = 55.83$ ;  $\text{H} = 6.45$ .

0.4235 „ 0.1160  $\text{AgBr}$ .  $\text{Br} = 11.65$ .

$\text{C}_{32}\text{H}_{45}\text{O}_9\text{N} \cdot \text{HBr} + \text{H}_2\text{O}$  requires  $\text{C} = 55.97$ ;  $\text{H} = 6.99$ ;  $\text{Br} = 11.66$  per cent.

Unsuccessful attempts were made to prepare an anhydrous hydrobromide by a direct method.

*Pyrojapaconitine aurichloride* is precipitated in bulky, yellow flocks on the addition of aqueous auric chloride to an aqueous solution of pyrojapaconitine hydrochloride. It crystallises very easily from its solution in alcohol or chloroform after either spontaneous evaporation or the addition of ether. The melting point of the salt varies with the solvents from which it is crystallised, that from chloroform melting at about  $160$ — $161^\circ$ , and that from alcohol and ether at about  $188$ — $189^\circ$ .

The following results were obtained by the analysis of the salt (m. p. 160—161°) crystallised from chloroform:

0.3389 gave 0.0697 Au and 0.2025 AgCl. Au = 20.56; Cl = 14.78.

The salt (m. p. 188—189°) crystallised from alcohol and ether gave the following data:

0.1742 gave 0.2556 CO<sub>2</sub> and 0.0740 H<sub>2</sub>O. C = 40.01; H = 4.72.

0.1694 „ 0.2502 CO<sub>2</sub> „ 0.0696 H<sub>2</sub>O. C = 40.28; H = 4.56.

C<sub>32</sub>H<sub>45</sub>O<sub>9</sub>N, HAuCl<sub>4</sub> + H<sub>2</sub>O requires C = 40.63; H = 5.07; Au = 20.84;  
Cl = 15.02 per cent.

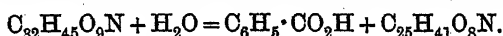
C<sub>32</sub>H<sub>45</sub>O<sub>9</sub>N, HAuCl<sub>4</sub> requires C = 41.42; H = 4.96; Au = 21.25;  
Cl = 15.31 per cent.

No aurichlor derivative could be obtained.

## V. PYROJAPACONITINE.

### *Hydrolysis of Pyrojapaconitine.*

Pyrojapaconitine is hydrolysed with extreme readiness by alkalis, the hydrolysis being complete in less than an hour. The products of the reaction are benzoic acid and a new base, *pyrojapaconine*,



Pyrojapaconine may be extracted from its aqueous alkaline solution by shaking either with ether or chloroform, preferably the latter. Light petroleum precipitates the substance from the ethereal solution in colourless, amorphous flakes melting at about 123—128°. The base is very deliquescent.

Its specific rotation is  $-73.96^\circ$ .

$$\alpha_D^{25} = -4.3^\circ; l = 2 \text{ dm.}; c = 2.9106; [\alpha]_D^{25} = 73.96^\circ.$$

Combustions of pyrojapaconine furnished the following results:

0.1495 gave 0.3385 CO<sub>2</sub> and 0.1060 H<sub>2</sub>O. C = 61.75; H = 7.87.

0.1499 „ 0.3370 CO<sub>2</sub> „ 0.1035 H<sub>2</sub>O. C = 61.31; H = 7.67.

C<sub>25</sub>H<sub>41</sub>O<sub>8</sub>N requires C = 62.11; H = 8.48 per cent.

All attempts to crystallise either the base or its salts were unsuccessful. The *aurichloride* is soluble in warm water, but separates in a vitreous mass on cooling. It is soluble in alcohol, and the deep yellow solution becomes colourless after long standing.

## VI. THE AMORPHOUS ALKALOIDS OF JAPANESE ACONITE.

In working up the crystalline japaconitine used for the preceding work, a small amount of an amorphous base was accumulated. This base furnished a hydrochloride, which crystallised readily from



water in the minute crystals so characteristic of japbenzaconine hydrochloride, and melted at 241—242°. By recrystallisation from alcohol and ether, the melting point was raised to 245°. This is the melting point of japbenzaconine hydrochloride. In order to completely confirm the identity of this substance, a small quantity was converted into the aurichlor derivative by adding light petroleum to an alcoholic solution of the aurichloride. Colourless octahedra of *aurichlor-japbenzaconine* melting at 179° separated. The amorphous base which accompanies japaconitine in Japanese aconite roots is therefore japbenzaconine. The amount is exceedingly small (about 1 gram from 11½ kilos.) as compared with the quantity of benzaconine contained in the roots of *Aconitum Napellus*.

The results of this investigation, which has occupied us for several years, seem to leave no room for doubt that the crystalline alkaloid (japaconitine) of Japanese aconite, though closely resembling aconitine, the crystalline alkaloid of *A. Napellus*, is chemically a distinct individual. The chief differences which we have established between them and their derivatives are summarised in the following tables :

I.—*Japaconitine and Aconitine.*

Substance.	Melting point.	Specific rotation.	Remarks.
Japaconitine .....	204·2°	+20·25° in chloroform	Prismatic needles
Aconitine .....	196—197°	+14·6° in chloroform	Hexagonal prisms
Japaconitine hydrochloride...	149—150°	—23·8° in water	
Aconitine hydrochloride .....	149°	—30·9° in water	
Japaconitine hydrobromide...	172—173°		
Aconitine hydrobromide .....	163°	—30·8° in water	
Japaconitine hydriodide .....	207—208°		
Aconitine hydriodide .....	226°		
Japaconitine aurichloride ...	{ (α) 153° (β) 231°		
Aconitine aurichloride .....	{ (α) 185·5° (β) 152° (γ) 176°		
Triacetyljapaconitine .....	166—167°		
Triacetylaconitine .....	207°		

II.—*Japbenzaconine and Benzaconine.*

Substance.	Melting point.	Specific rotation.	Remarks.
Japbenzaconine .....	182—183°	+40·16° in alcohol	Rectangular plates Uncrystallised
Benzaconine .....	125°	+4·48° in alcohol	
Japbenzaconine hydrochloride	253°	-19·73° in water	
Benzaconine hydrochloride ...	{(a) 217° (β) 268°}	-28·7° in water	
Japbenzaconine hydrobromide	205—217°		
Benzaconine hydrobromide...	282°		
Japbenzaconine aurichloride..	228°		
Benzaconine aurichloride.....	125—135°		
Aurichlor-japbenzaconine.....	178°		Octahedra Rectangular prisms
Aurichlor-benzaconine .. .....	204°		

*Japaconine and Aconine.*

Substance.	Melting point.	Specific rotation.	Remarks.
Japaconine .....	97—100°	+10·88° in water	Amorphous, very hygroscopic Aconine ....., very hygroscopic
Aconine .....	132°	+23° in water	
Japaconine hydrobromide ...	221°		
Japaconine hydrochloride ...			Uncrystallised
Aconine hydrochloride.....	175·5°	-7·71° in water	

*Pyrojapaconitine and Pyraconitine.*

Substance.	Melting point.	Specific rotation.	Remarks.
Pyrojapaconitine .....	153—168°	— 65·89° in alcohol	
Pyraconitine <sub>2</sub> .....	167·5°	Inactive	
Pyrojapaconitine hydrochloride	175—176°		
Pyraconitine hydrochloride...	248·75°		
Pyrojapaconitine hydrobromide	{(α) 208°}	— 102·5°	
	{(β) 241°}		
Pyraconitine hydrobromide...	{(α) 204°}	— 46·8° in water	
	{(β) 280°}		
Pyrojapaconitine aurichloride	161°		Crystalline
Pyraconitine aurichloride.....			Uncrystallised
Pyrojapaconine .....		— 73·96° in water	Uncrystallised
Pyraconine.....		— 90·99° in water	Uncrystallised

The conclusions to be drawn from our results as to the composition and properties of japaconitine are not in agreement with those of Wright and his fellow-workers. Neither can we confirm the opinions which have been advanced by Mandelin, Lübke, and by Freund and Beck, all of whom regard japaconitine as identical with aconitine.

For the present, we reserve a discussion of the exact nature of the relationship between japaconitine and aconitine, as we are not yet in a position to decide finally which formula to select for either alkaloid as most correctly expressing its composition and the composition of its derivatives.

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## VI.—*A Method of Separation of the various Isomerides contained in ordinary commercial Xylidine.\**

By W. R. HODGKINSON and LEONHARD LIMPACH.

ORDINARY technical, or commercial, xylidine, obtained by the nitration and subsequent reduction of the coal tar xylene distilling between

\* This is a continuation of some work on xylidines and xylenols (compare Trans., 1892, 61, 420; 1893, 63, 104).

136° and 142°, contains, with the exception of the symmetrical 5-amino-*m*-xylene, all the possible isomerides from the three xylenes. The main constituents are the 4-amino-*m*-xylene and the 2-amino-*p*-xylene, which together make up about 70 per cent. of the total bases.

In the present paper, an account is given of a process for effecting a complete separation of all the isomerides present in commercial xylidine, making use of the method already devised by one of the authors for the isolation of 4-amino-*m*-xylene as acetate, and of 2-amino-*p*-xylene as hydrochloride (Germ. pat., 39947, of September 19th, 1886; Eng. pat., 11822, 1886), and of 2-amino-*m*-xylene by means of its formyl derivative (*Ber.*, 1899, 32, 1008).

#### *4-Amino-m-xylene.*

When acetic acid is added to ordinary xylidine, the acetate of the 4-amino-*m*-xylene is the *only one* to crystallise out. The method we have worked out, and employed to obtain the different xylenols, depends in the first instance on this fact.

As an example, 300 grams of commercially pure xylidine were treated with slightly more than the necessary amount of glacial\* acetic acid to convert the 4-amino-*m*-xylene into its acetate.† The crystallisation of the acetate commenced at once, and was practically completed after 24 hours standing. The crystals were separated in a centrifugal separator (a filter pump would be equally effective), and, after pressing, were found to be almost pure 4-amino-*m*-xylene acetate. As a rule, the yield of the base by this method amounts to from 40 to 42 per cent. of the original xylidine.

The acetate was hydrolysed with sodium hydroxide, and the base converted into the formyl derivative, which, after the first crystallisation from dilute alcohol, melted at 113.5°.

#### *2-Amino-p-xylene.*

The filtrate and mother liquors contain a considerable amount of the 2-amino-*p*-xylene‡ and smaller quantities of 3-amino-*o*-xylene, 4-amino-*o*-xylene, and 2-amino-*m*-xylene.

To this mixture, hydrogen chloride (ordinary strong solution) was added until the whole dissolved. On cooling, the 2-amino-*p*-xylene hydrochloride crystallised out, and after a couple of recrystallisations was obtained quite pure.

\* Glacial acid is not absolutely necessary; 80 per cent. acid acts quite well, but the product takes a longer time to crystallise.

† This can be ascertained sufficiently nearly on a very small scale.

‡ This is valuable for the production of pseudocumidine.

It may be remarked that the product obtained in the first crystallisation is sufficiently pure for conversion into pseudocumidine.

Some of the product from the first crystallisation was made into the formyl derivative. This melted at 116—117°, after the first crystallisation from weak alcohol.

As indicated by this method, about 30 per cent. of this isomeride is, as a rule, contained in ordinary xylidine.

### *2-Amino-m-xylene.*

The residue (filtrate) from the para-base now contains the two ortho- and the meta-isomerides. We find that the 2-amino-*m*-xylene can be very completely separated in the following manner. The mother liquors are evaporated in a retort. After the excess of acid and water has distilled off, the contents of the retort become semi-solid. On now gently heating, the hydrochloride of 2-amino-*m*-xylene sublimes in very beautiful, silky, needle-shaped crystals. One re-sublimation gave a perfectly pure product. From 300 grams of xylidine we have obtained 10.6 grams of this salt, indicating the presence of 2.7 per cent. of this isomeride.

Another method, adapted for larger operations, is to distil off about 20 per cent. of the contents of the retort by heating rapidly; the distillate then solidifies very quickly. It can then be converted into the formyl derivative, and easily be obtained perfectly pure by one crystallisation.

The formyl derivative of 2-amino-*m*-xylene crystallises in very beautiful, long needles which, when slowly heated in the usual way, melt at 164°, but when rapidly heated, melt only at 176—177°. It is completely hydrolysed after boiling for 6 hours with alcoholic potassium hydroxide.

The acetyl derivative melts at 177°, and also crystallises in long needles.

The base distils completely at 216° under 735 mm. pressure (therm. in vapour), and has a sp. gr. 0.980 at 15°.

From this isomeride, we have obtained, by diazotisation, the *m*-2-xenol.\* It crystallises from water, in which it is somewhat soluble, in long, hard crystals, and from dilute alcohol in long prisms. It melts at 47° and boils at 199.5° (therm. in vapour) under 738 mm. pressure.

\* We have prepared a number of derivatives from this xenol, which we hope to describe, with others, later.

*3-Amino-o-xylene.*

The black residue in the retort, from which the 2-amino-*m*-xylene hydrochloride had been sublimed, consisted of the hydrochlorides \* of the two ortho-bases.† It was dissolved in water, and the bases, set free by the addition of excess of sodium hydroxide, were separated from the alkaline liquid, distilled in steam,‡ and then converted into their formyl derivatives. This is particularly easily accomplished by the simple addition of the necessary amount of formic acid, of 25 per cent. strength, and heating on a water-bath.

The two formyl compounds were now separated by taking advantage of a slight difference in their rate or facility of crystallising. After standing for a few days, the mixture became semi-solid; the liquid portion was then pressed out, and the solid portion recrystallised. The first batch of crystals melted at 100–102°. They were hydrolysed by alcoholic sodium hydroxide, and the base converted into the acetyl derivative, which melted at 132°.

This base, therefore, is 3-amino-*o*-xylene, and the amount contained in xylidine amounts roughly to 9–11 per cent.

*4-Amino-o-xylene.*

The mother liquor pressed from the formyl derivative of 3-amino-*o*-xylene consists for the most part of that of 4-amino-*o*-xylene, with small quantities of the other bases which have escaped separation.

It is very difficult to induce this formyl derivative to crystallise. Cooling with a freezing mixture to  $-20^{\circ}$  for some time was without result. It was therefore hydrolysed, and the base separated. This distilled over completely at 222° (therm. in vapour), and after standing for 3 or 4 months during the winter, formed large, monoclinic crystals, which melted at 48°. A formyl derivative prepared from them was induced to crystallise by considerable cooling and agitation, and the base obtained from this crystallised material by hydrolysis melted at 52°. There is therefore no doubt it is the 4-amino-*o*-xylene.

We have prepared considerable quantities of the xylenols corresponding to these xylidines, and will shortly give an account of some of their derivatives.

WOOLWICH AND ERLANGEN.

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\* For some purposes these may be used without further purification.

† About 20 to 25 per cent. of these isomerides is contained in ordinary xylidine.

‡ These bases also distil alone without decomposition.

## VII.—*The Oxidation of Organic Acids in Presence of Ferrous Iron. Part I.*

By HENRY J. HORSTMAN FENTON, M.A., F.R.S., and H. O. JONES,  
B.A., B.Sc.

THE oxidation of various organic substances by means of hydrogen dioxide and other agents in presence of small quantities of iron salts, has formed the subject of a considerable number of communications to the Society and elsewhere (compare Fenton, *Chem. News.*, 1876, 33, 190; 1881, 43, 110; *Trans.*, 1894, 65, 899; 1896, 69, 546; *Proc.*, 1898, 14, 119; *Brit. Assoc. Reports*, 1895, 1898, 1899; Fenton and Jackson, *Trans.*, 1899, 75, 1; Cross and Bevan, *Trans.*, 1898, 73, 463; 1899, 75, 747; Morrell and Crofts, *Trans.*, 1899, 75, 786; Martinon, *Bull. Soc. Chim.*, 1885, [ii], 23, 196).

The present paper deals with a continuation of this investigation, which is being carried out by the authors with a view of arriving at further general conclusions as to the nature of the reaction, the subjects selected for examination being various acids of typical constitution.

Hydrogen dioxide has been employed as the oxidising agent in quantities corresponding to one atom of oxygen, or less, per molecule of acid, and the experiments have been carried out at low temperatures ( $0^{\circ}$  to  $15^{\circ}$ ). Larger proportions of oxygen and higher temperatures will probably give rise to interesting modifications in the results, and these will be studied on a future occasion. The iron, which is always used in the ferrous condition, is generally added as a salt of the acid operated upon, but in some cases ferrous sulphate or acetate is employed.

The following is a brief outline of the method employed in carrying out the initial experiments:

I. The acid (1 mol.) was dissolved in, or in some cases mixed with, a small quantity of water, cooled by ice, and hydrogen dioxide was added in proportion corresponding to about  $\frac{1}{2}$  at. of oxygen.

II. The experiment was repeated under exactly similar conditions, but, with the previous addition of ferrous sulphate solution corresponding to  $\frac{1}{2}$  at. of iron, the dioxide being added in quantity corresponding to about  $\frac{1}{2}$  at. of oxygen in excess of that required to oxidise the iron.

The mixtures were kept in ice and tested for free hydrogen dioxide after five minutes and again after thirty minutes, chromic acid or titanous acid being used for this purpose.

With the following acids, strongly marked indications of free

hydrogen dioxide were shown in both series of experiments even after 30 minutes: *acetic, monochloracetic, oxalic, malonic, succinic, dibromosuccinic, fumaric, maleic*. Considering the small proportion of dioxide employed, these acids may therefore be considered, at any rate for the present purpose, as inactive towards the reagent.

In the case of *formic, glycollic, lactic, glyceric, tartronic,  $\beta$ -hydroxybutyric, tartaric, malic, saccharic, mucic, pyromucic, acetylenedicarboxylic, acetonedicarboxylic, dihydroxytartaric, dihydroxymaleic, benzoic*, and *picric* acids, however, a rapid (generally almost instantaneous) oxidation takes place in experiment II, that is, in the presence of the ferrous salt, all traces of the dioxide disappearing within five minutes, whereas in experiment I, where iron is absent, strongly marked indications of the dioxide remain after 30 minutes. *Citric* and  *$\beta$ -iodopropionic* acids behave similarly, but the oxidation in presence of iron is less rapid.

*Pyruvic* acid alone appears to be immediately attacked by hydrogen dioxide, either *with* or *without* the presence of iron.

In the case of nearly all of the above acids which are 'active' towards the reagent, the products appear to be of great interest, new substances being obtained or oxidations effected which are not possible by other means. The systematic study of these changes, although in some cases direct and simple, yet often, in others, presents peculiar difficulties owing to the unstable nature of the products.\* It is evident, therefore, that the complete investigation of these products, together with those of several other acids which suggest themselves, will occupy a very considerable time, and it is considered desirable in the present communication to give an account of results which have been obtained up to the present date.

#### *Glycollic Acid.*

The pure crystallised acid (1 mol.) was dissolved in water, mixed with a small quantity of ferrous acetate ( $\frac{1}{2}$  at. or less of Fe), the mixture cooled by ice, and hydrogen dioxide (1 at. of oxygen) slowly added. On addition of phenylhydrazine acetate (1 mol.), a dark coloured precipitate is immediately formed, which soon turns orange-red and increases considerably in quantity on standing. This precipitate was washed, dried, and purified first by crystallisation from a mixture of ether and light petroleum, and then from a small quantity of hot ethyl acetate (a small quantity of light yellow, insoluble matter remains which appears to be ferrous oxalate). This product crystallises in orange-yellow needles which melt and decompose at

\* Compare, for example, the identification and isolation of dihydroxymaleic acid (Trans., 1894, 65, 899 *et seq.*).



137°, and corresponds entirely with the hydrazone of *glyoxylic acid*,  $\text{CH}(\text{N}_2\text{H}\cdot\text{C}_6\text{H}_5)\cdot\text{CO}_2\text{H}$ , which was prepared by Elbers from calcium glyoxylate (*Annalen*, 1885, 227, 341).

0.2120 gave 31.7 c.c. nitrogen at 18° and 752 mm.  $\text{N} = 17.30$ .

$\text{C}_8\text{H}_8\text{O}_2\text{N}_2$  requires  $\text{N} = 17.07$  per cent.

The yield of crude hydrazone is nearly equal to the weight of acid used.

#### *Lactic Acid.*

When this acid is oxidised in a similar manner, a very considerable evolution of heat occurs, and, in order to obtain the best results, it is necessary to add the oxidising agent very slowly, and to take especial care to keep the mixture cold; it was found advisable also to use only about one-half the calculated quantity of oxygen. The reason that these precautions are necessary is probably to be found in the great instability of the product towards hydrogen dioxide (see pyruvic acid).

On adding phenylhydrazine acetate (1 mol. in proportion to the dioxide employed), a greenish or yellow precipitate of pyruvic acid hydrazone,  $\text{CH}_3\cdot\text{C}(\text{N}_2\text{H}\cdot\text{C}_6\text{H}_5)\cdot\text{CO}_2\text{H}$ , is obtained, which, when washed with a little cold alcohol and recrystallised from hot alcohol, separates in the form of long, pale yellow, transparent needles, which, when quickly heated, melt at 192°.

0.2102 gave 29.1 c.c. nitrogen at 22° and 758.3 mm.  $\text{N} = 16.03$ .

$\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$  requires  $\text{N} = 15.73$  per cent.

#### *Tartronic Acid.*

This was prepared from dihydroxytartaric acid in the manner previously described by one of the authors (*Trans.*, 1898, 73, 72). The aqueous solution was mixed with ferrous sulphate ( $\frac{1}{4}$  at. Fe) and hydrogen dioxide corresponding to rather less than 1 at. of oxygen slowly added. On the addition of phenylhydrazine hydrochloride (1 mol. in proportion to the oxygen employed) a bulky, brownish-yellow precipitate of mesoxalic acid hydrazone,  $\text{O}(\text{CO}_2\text{H})_2\cdot\text{N}_2\text{H}\cdot\text{C}_6\text{H}_5$ , was obtained. This, when recrystallised from hot alcohol, was obtained in long, transparent, pale yellow prisms, which melted at 170—171° when quickly heated.\* The yield of hydrazone is nearly equal to the weight of acid oxidised.

0.2342 gave 27.5 c.c. nitrogen at 20.5° and 753 mm.  $\text{N} = 13.57$ .

$\text{C}_9\text{H}_8\text{O}_4\text{N}_2$  requires  $\text{N} = 13.46$  per cent.

\* Elbers (*loc. cit.*, 355) gives the melting point of this hydrazone as 158—164°, but Clemm (*Ber.*, 1898, 31, 1451) found that, if quickly heated, it melts at 174°.

The direct oxidation of tartronic to mesoxalic acid has not hitherto been effected, although of course the converse change is well known. It is possible that the process may be found advantageous for the preparation of mesoxalic acid, especially since tartronic acid is so easily obtained by the method above mentioned.

### *Glyceric Acid.*

The pure acid, free from glycerol, was oxidised in the manner above described, the iron being added in the form of ferrous glycerate. The action is immediate, and but little heat is evolved. One mol. of hydrogen dioxide appears to be used up almost quantitatively since, on the addition of any further quantity, but not before, the free dioxide can be detected in the mixture.

The resulting solution, when made alkaline with caustic soda, gives a beautiful *violet* colour, which is much intensified on the addition of ferric chloride. Treated with a mixture of alcohol and ether, the iron is nearly wholly precipitated, and the solution, on evaporation, leaves a thick syrup, which, when made alkaline, gives again the violet colour with ferric chloride. The substance, purified in this way, reduces ammoniacal silver nitrate, very slowly restores the colour to a rosaniline salt bleached by sulphurous acid, and gives precipitates with lead, barium, and silver salts.

On adding phenylhydrazine acetate (1 mol.), a bulky, orange precipitate is at once produced. The yield of crude substance (air-dried) is about equal to the weight of acid oxidised. It was purified by washing with a little cold benzene and recrystallising from hot benzene, from which it separates in aggregates of short prisms which melt at 203—205°. These, on analysis, gave  $N = 19.5$  per cent. The specimen prepared in this way, however, was found to contain a trace of iron, so that for further analysis it was purified by the method mentioned below.

On heating the substance with a strong solution of sodium carbonate, it dissolves to a yellow solution which dyes wool, &c., a bright lemon-yellow colour. Beautiful, yellow glistening plates or needles separate as the solution cools, and these, when dried at 100°, melted at 235—237°.

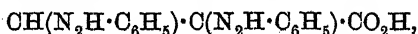
On decomposing this sodium compound with hot dilute hydrochloric acid, the original substance separates as an orange precipitate which, when recrystallised from hot benzene, melts at 207°. Dried at 100° it gave, on analysis, the following results:

0.1201 gave 0.2817  $CO_2$  and 0.0532  $H_2O$ .  $C = 63.96$ ;  $H = 4.92$ .

0.1295 „ 22.5 c.c. nitrogen at 19° and 760 mm.  $N = 20.37$ .

$C_{15}H_{14}N_4O_2$  requires  $C = 63.82$ ;  $H = 4.96$ ;  $N = 19.85$  per cent.

Nastvogel (*Annalen*, 1888, 248, 85) obtained a substance of this composition by acting upon dibromopyruvic acid (1 mol.) with phenylhydrazine (2 mols.). It formed orange crystals which melted at 201—203°, and its properties exactly corresponded to those of the substance obtained in the present case. The sodium salt was obtained in a similar way, and melted at 231°. From its mode of formation and properties, he assigned to it the formula -



and termed it the osazone of glyoxal-carboxylic acid.

Later, W. Will (*Ber.*, 1891, 24, 400) obtained this osazone in an entirely different way. He treated a solution of collodion-wool in alcoholic ether with a 10 per cent. solution of caustic soda for about 24 hours at 20°, and obtained an acid which had reducing properties, and, with phenylhydrazine acetate, gave an osazone, melting at 205°, identical with the above. Analysis of the calcium, strontium, and other salts of the acid indicated the formula  $\text{C}_8\text{H}_4\text{O}_4$  for the latter, so that it must be either hydroxypyruvic acid,  $\text{CH}_2(\text{OH})\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , or the semi-aldehyde of tartronic acid,  $\text{CHO}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , either of which would, of course, give the osazone in question. From the facts that the acid is not oxidised by bromine, and that it is not altered by heating with lime water or baryta water, Will concluded that it is hydroxypyruvic acid.

By acting upon an alcoholic solution of the osazone with hydrogen chloride, he obtained a substance crystallising in reddish-yellow needles and melting at 149°, which at first was considered to be the ethyl ester, but later (*loc. cit.*, 3831) was shown to be a pyrazolone derivative,  $\text{NHPh}\cdot\text{N}:\text{C} \begin{matrix} \text{CO}\cdot\text{NPh} \\ \text{CH}:\text{N} \end{matrix}$ . It is, in fact, identical with the phenylhydrazine ketophenylpyrazolone which Knorr obtained by heating the osazone with acetic anhydride (*Ber.*, 1888, 21, 1201).

In order further to confirm the identity of the osazone at present under consideration with that of Nastvogel and Will, it was converted into the pyrazolone by the method employed by the latter. The alcoholic solution of the osazone was saturated with dry hydrogen chloride, allowed to stand for some time, evaporated to dryness on a water-bath dissolved in dilute soda solution, filtered, and acidified with dilute sulphuric acid. The precipitated substance, on recrystallisation from alcohol, was obtained in beautiful orange needles melting at 148°.

From these results, it is evident that the oxidation product of glyceric acid may be either (1) the semi-aldehyde of tartronic acid, (2) hydroxypyruvic acid, or (3) the semi-aldehyde of mesoxalic acid. In order to throw further light upon the question, a solution of the oxidised product, prepared from a known weight of glyceric acid, was

mixed with a quantity of bromine corresponding to more than 2 atomic proportions in excess of that required to oxidise the iron present. After standing for 24 hours at the ordinary temperature, with repeated shaking, the free bromine was removed by sulphurous acid, and sodium acetate and phenylhydrazine acetate added. The resulting precipitate was found to be identical in every respect with that originally obtained, and the yield was but little diminished. Further experiments were made, using a considerably larger excess of bromine, and also allowing the mixture to stand for over a fortnight, but in all cases the resulting liquid gave strong evidence of the presence of the original substance, an intense violet colour being obtained on testing the mixture with ferric chloride and alkali after removal of the free bromine. It appears therefore that the substance is incapable of oxidation by bromine, in presence of water, at the ordinary temperature. Heated with bromine on a water-bath for several hours, the substance is slowly oxidised; the resulting product has not been fully examined, but appears to be neither tartronic nor mesoxalic acid.

With excess of freshly precipitated silver oxide, again, very little oxidation results at the ordinary temperature, the mixture, even after standing for some days and subsequent removal of the silver, showing a strong reaction with ferric chloride and giving the same osazone with phenylhydrazine. When heated for some time at about  $40^{\circ}$ , the oxidation proceeds more quickly, but the product, after removal of silver, appears to be only oxalic acid. A copious precipitate of phenylhydrazine oxalate is obtained on adding the acetate, whereas the hydrochloride gives only a slight precipitate resembling the original osazone.

If the original solution (containing iron) is mixed with a large excess of baryta water, the violet precipitate which is formed remains permanent, even on heating for two or three hours on a water-bath.

These facts afford fairly strong evidence that the oxidation product is not aldehydic, and consequently that the acid under consideration is *hydroxypyruvic acid*. The *absence* of the other two acids in minute quantity is of course not absolutely certain, since small traces of tartronic or mesoxalic acids might not be detected in the products mentioned.

The properties of the substance coincide in fact very closely with those of the acid obtained by Will from collodion. In Will's papers, however, no mention is made of the remarkable colour reaction with ferric chloride, which is certainly the most striking property of the present substance. This colour reaction is very similar to that produced by dihydroxymaleic acid, and the authors were at first inclined to believe that the product might be dihydroxyacrylic acid,  $\text{CH}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$ , which would be formed from glyceric acid by

removal of two non-hydroxylic hydrogen atoms (compare Proc., 1898, 14, 119). It is of course possible that this may represent the initial reaction and that the product afterwards undergoes tautomeric change, becoming hydroxypyruvic acid.

#### *Malic Acid.*

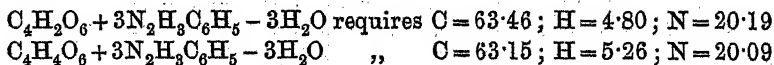
On addition of hydrogen dioxide to a solution of this acid containing a little ferrous salt, the colour of the liquid immediately becomes deep red, much heat is evolved, and carbon dioxide is given off. If, however, the solution is carefully cooled by a freezing mixture and the hydrogen dioxide added very slowly, the action proceeds without any appreciable evolution of gas. In the following experiments, the acid was dissolved in very little water and the required quantity of iron (*ferrum redactum* about  $\frac{1}{2}$  at.) dissolved in the liquid.\* The hydrogen dioxide was used in quantity representing rather less than 1 at. of oxygen.

On adding phenylhydrazine acetate (1 mol. in proportion to the oxygen employed) to the resulting liquid, a very copious, bright, orange-yellow precipitate is formed *immediately*. The yield of this precipitate (air dried) considerably exceeds the weight of acid oxidised. This substance dissolves sparingly in most cold solvents, but fairly easily in hot alcohol, benzene, or chloroform. It may be crystallised from any of these solvents, but the last appears to give the best result. It is thus obtained in brilliant, long, orange-yellow prisms belonging to the prismatic system, and melting at 217—219°.

Distinct specimens prepared on different occasions, and all melting within the above range of temperature, gave the following results on analysis:

I. C = 63.30.	H = 5.17.	N = 20.10.
II. C = 63.35.	H = 5.47.	N = 20.21.
III. C = 62.87.	H = 4.95.	N = 20.07.
IV. C = 63.31.	H = 5.12.	N = 20.26.

Assuming that the product is derived from an acid containing four carbon atoms these numbers correspond best with those required for a derivative of dihydroxytartaric acid or of dihydroxymaleic (or isomeric) acid.



It will be shown in the following communication (p. 81) that this substance is the result of further action of the oxidising agent upon the product which is first formed. It was evident, in fact, that the action

\* It is now found, however, that the addition of ferrous sulphate or acetate answers equally well.

of phenylhydrazine does not in this case afford direct evidence as to the nature of the reaction under investigation, and the problem was therefore attacked in a different manner. The experiments which were made resulted in the isolation of *oxalacetic acid*, and from the special interest which attaches to this substance, the authors have thought it advisable to give an account of this part of the investigation in a separate paper.

The following acids have been only superficially examined :

*Mucic* and *Saccharic Acids*, when oxidised in the above manner, yield products which give brown precipitates with phenylhydrazine acetate, and when made alkaline with caustic soda give deep red-violet colours, which are intensified by the addition of ferric chloride. If the action is analogous to that of tartaric acid, it is evident that these products may be of much interest. They are very unstable, however, and it will doubtless be a matter of some difficulty to isolate them.

*Pyromucic Acid* turns an intense but transient violet colour, and *picric acid* gives an intense green colour; both products react with phenylhydrazine.

*Acetylenedicarboxylic Acid* is immediately attacked in presence of iron—the solution becoming dark brown. The solution now gives an immediate precipitate with phenylhydrazine, which is quite different from the precipitate slowly formed with the original acid.

*Acetonedicarboxylic Acid*.—This is similarly oxidised when iron is present, the change taking place rather more slowly than in the preceding cases. The product gives an intense purple colour with alkalis, which is intensified on addition of ferric chloride. This colour is quite distinct from that given by the original acid with ferric chloride, which is destroyed by alkalis.

*Benzoic Acid* is immediately oxidised, the result giving a violet colour with ferric salts, presumably due to the formation of salicylic acid.

It is the intention of the authors to make a complete study of these products, and to extend the observations to a large number of other acids. It is evident that several general conclusions might already be suggested by the foregoing results, but it is considered preferable to defer such considerations until the investigation is completed.

Part of the expenditure which has been incurred in carrying out this research has been defrayed by funds kindly placed at the disposal of one of the authors by the Government Grant Committee of the Royal Society.

VIII.—*Oxalacetic Acid.*

By HENRY J. HORSTMAN FENTON, M.A., F.R.S., and H. O. JONES,  
B.A., B.Sc.

IN the preceding communication, it is shown that malic acid is very energetically oxidised by hydrogen dioxide in presence of ferrous iron. The oxidation is attended with considerable evolution of heat, and unless special precautions are taken to keep the temperature low, carbon dioxide is evolved and pyruvic acid is found in the liquid.

On shaking up the original oxidised mixture with ether, scarcely anything could be extracted, and the addition of salt, sodium sulphate, &c., did not much improve the result. In the initial experiments, which were made in studying the oxidation product of tartaric acid (Trans., 1894, 65, 901), it was shown that the addition of strong sulphuric acid to the mixture greatly increased the yield on extraction with ether, and in the present instance the same is found to be the case. By adding slowly about one-tenth its volume of strong sulphuric acid to the oxidised mixture, with careful cooling, and repeatedly shaking with ether, a considerable quantity of substance can be extracted.

In the first experiments, no special care was taken to keep the mixture well cooled during oxidation and during the addition of sulphuric acid. In this case, the ether extract, on evaporation, gave a syrupy residue with a small quantity of a white, crystalline substance. The syrupy portion, when dissolved in water, gave immediately a white precipitate with phenylhydrazine acetate which, when recrystallised from alcohol, melted at  $192^{\circ}$ , and had all the characters of *pyruvic acid* hydrazone.

0.1494 gave 20.9 c.c. nitrogen at  $25^{\circ}$  and 749.4 mm.  $N = 15.85$ .

$C_9H_{10}O_2N_2$  requires  $N = 15.73$  per cent.

It was afterwards found that if great precautions are taken to prevent rise of temperature during the operations referred to, the ether extract, when concentrated to a small bulk, deposits the white, crystalline substance in considerable quantity, and, on further evaporation, usually solidifies to a white mass.

The method of proceeding is as follows: Malic acid (1 mol.) is dissolved in the least possible quantity of water, and a ferrous salt is added in quantity corresponding to about  $\frac{1}{8}$  at., or less, of iron. The nature of the ferrous salt is immaterial, and the sulphate, acetate, or malate may be employed. The mixture is cooled by ice and salt until

it begins to freeze, and hydrogen dioxide (20-volume strength\*), cooled in a similar way, is added in very small quantities at a time with careful mixing, in proportion amounting to nearly 1 at. of oxygen. The liquid assumes an intense blood-red colour as soon as the first few drops of the dioxide have been added. The solution is now mixed with about one-tenth of its volume of strong sulphuric acid, great precautions being taken, as before, to prevent the temperature from rising more than a few degrees, and is repeatedly extracted with ether. The ethereal solution gives an intense blood-red colour with ferric chloride, so that the progress of the extraction, is easily tested; even after 25 extractions, a further yield may be obtained.

The ethereal extract is concentrated to a small bulk and the residual solution, on cooling, begins to deposit the white, crystalline acid, the quantity being much increased on stirring. It is kept in a desiccator, partially exhausted, until the whole has solidified, and is then quickly washed three or four times with cold water, draining well each time with the aid of a pump. The yield of pure substance is about 22 per cent. of the acid oxidised.

*Properties.*—The substance separates from its solution in ether, acetone, or water, in white, crystalline aggregates which dissolve very slowly in cold water and easily, but with decomposition, in hot water. It is rather more soluble in ether, easily soluble in alcohol or acetone, and scarcely soluble in chloroform or benzene.

It crystallises from a mixture of acetone and benzene in blade-like crystals belonging to the prismatic system, and has a great tendency to form close aggregates. The aqueous solution gives an intense blood-red colour with ferric salts, which is scarcely affected by dilute mineral acids.

Heated in a capillary tube, it melts with sudden decomposition at 176—180°. Analysis of the substance dried in a vacuum desiccator gave the following result:

0.1766 gave 0.2361  $\text{CO}_2$  and 0.0488  $\text{H}_2\text{O}$ . C = 36.46; H = 3.07.

$\text{C}_4\text{H}_4\text{O}_5$  requires C = 36.36; H = 3.03 per cent.

Owing to its sparingly solubility in appropriate solvents, and to its instability at high temperatures, the molecular weight could not well be determined by the freezing or boiling point methods. It will be shown, however, that the methyl ester dissolves easily in acetic acid, so that the value is easily determined in that case.

*Titration with Alkalis.*—The acid was dissolved in cold water and

\* In later experiments, the dioxide has been allowed partially to freeze until the strength of the liquid portion is about doubled, and this procedure is found to be very advantageous, owing to the smaller quantity of water introduced.



titrated with pure caustic soda solution containing 0.01507 Na per c.c., prepared from metallic sodium. Phenolphthalein was used as indicator, and special precautions were taken to exclude carbon dioxide.

0.5188 required 11.85 c.c. soda solution for neutralisation, the calculated amount for a dibasic acid of the formula  $C_4H_4O_5$  being 11.99 c.c.

After boiling the aqueous solution for a few minutes, carbon dioxide is evolved and the neutralising power is nearly halved, thus 0.6097 gram of the substance was heated for 5 minutes and then required 8.2 c.c. of the alkali, the calculated amount being 7.0 c.c. After heating for half an hour, a nearly similar result was obtained. On acidifying the resulting solution with acetic acid and adding phenylhydrazine acetate, a nearly white, crystalline precipitate was obtained which melted at  $192^\circ$ , and had all the other characters of *pyruvic acid hydrazone*.

*Barium Salt*.—A solution of the acid was exactly neutralised with pure soda and an excess of barium chloride added. The resulting white precipitate was well washed and dried in a vacuum desiccator.

0.4780 gave 0.3677  $BaSO_4$ .  $Ba = 45.23$ .

$C_4H_4O_5Ba + 2H_2O$  requires  $Ba = 45.21$  per cent.

This salt, when treated with ferric chloride, gives a deep, brick-red colour.

Calcium, strontium, lead, and silver salts, similarly, give white precipitates, the silver salt being quickly reduced on heating.

*Methyl ester*,  $C_2H_2O(CO_2CH_3)_2$ .—This was obtained by dissolving the acid in methyl alcohol, cooling the solution by ice, and partially saturating with dry hydrogen chloride. After the mixture had remained for about 24 hours, it was allowed to evaporate over solid potash and sulphuric acid, and the resulting solid crystalline mass well washed with cold water, in which it is scarcely soluble, then with a little cold methyl alcohol, and was finally recrystallised from hot methyl alcohol. It is thus obtained in beautiful, transparent, oblique prisms which melt at  $77^\circ$ .

The following results were obtained on analysing the substance dried in a vacuum desiccator :

- I. 0.1418 gave 0.2334  $CO_2$  and 0.0607  $H_2O$ .  $C = 44.89$ ;  $H = 4.75$ .  
 II. 0.1571 „ 0.2598  $CO_2$  „ 0.0712  $H_2O$ .  $C = 45.10$ ;  $H = 5.03$ .  
 $C_6H_8O_6$  requires  $C = 45.00$ ;  $H = 5.00$  per cent.

Three molecular weight determinations by the freezing point method in the same quantity of acetic acid gave the following numbers, the calculated molecular weight being 160 :

	Solvent.	Substance.	Depression.	Mol. weight.
I.	13.90	0.1290	0.243	148.9
II.	—	0.2908	0.532	153.3
III.	—	0.4038	0.753	150.5

The alcoholic solution of this ester gives the deep red colour with ferric chloride.

The analysis, molecular weight, melting point, and other properties show that this substance is identical in every way with *methyl oxalacetate*, which was obtained by Wislicenus from the action of sodium on a mixture of oxalic and acetic esters, the melting point of which is given as 74—76°.

*Action of Phenylhydrazine on the Acid.*

When the acid (1 mol.) is dissolved in a little cold water and mixed with phenylhydrazine acetate (1 mol.), the solution at first remains clear, but after standing for some minutes it gives, on stirring, a pale, straw-coloured, crystalline precipitate of the *hydrazone of oxalacetic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}(\text{N}_2\text{H}\cdot\text{C}_6\text{H}_5)\cdot\text{CO}_2\text{H}$ , which is seen under the microscope to consist of transparent, oblique prisms. This product is nearly pure, giving, on analysis, N = 12.14 per cent. After recrystallisation from cold, dry ether, however, the crystals are lustrous and perfectly colourless. After drying in a vacuum desiccator, they yielded the following results on analysis:

0.1232 gave 0.2422  $\text{CO}_2$  and 0.0499  $\text{H}_2\text{O}$ . C = 53.61; H = 4.50.

0.1841 „ 19.3 c.c. nitrogen at 17° and 767 mm. N = 12.49.

$\text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_2$  requires C = 54.05; H = 4.50; N = 12.61 per cent.

The pure substance, when slowly heated, turns yellow, and without melting shows signs of decomposition at 95—100°; if suddenly heated to a little above 100°, the decomposition is violent. The yellow product of decomposition, however, melts at 182—183°.

This hydrazone dissolves in concentrated sulphuric acid with a deep red colour, and on addition of ferric chloride to the solution a fine purple colour is produced. It resembles in this respect the hydrazone of the methyl ester.

Wislicenus (*Ber.*, 1886, 19, 3225) and Buchner (*Ber.*, 1889, 22, 2929) have shown that the hydrazones of ethyl and methyl oxalacetates when acted on by dilute alkalis or acids, lose the respective alcohol and water, giving rise to a sparingly soluble acid having the formula  $\text{C}_{10}\text{H}_8\text{O}_3\text{N}_2$ , which begins to decompose without melting at 240—250°, and melts at 263°. This substance is shown to be 1-phenyl-5-pyrazolone-3-monocarboxylic acid. This acid gave a

red colour with nitric acid, a scarlet with nitrous acid, and a dark blue with ferric chloride in hot aqueous solution.

It was considered probable therefore that the hydrazone at present under consideration might behave in a similar way, and such is found to be the case. On heating the original pale yellow substance with dilute sulphuric acid, it is changed in a few minutes into a voluminous, white, crystalline magma, which dissolves sparingly in boiling water, and separates on cooling in beautiful, transparent needles. On heating, these turned yellow and showed signs of decomposition at about 243°, and completely melted at about 260°. For analysis, the substance was dried at 100°.

0.1804 gave 21.2 c.c. nitrogen at 18.5° and 764 mm.  $N = 13.88$ .

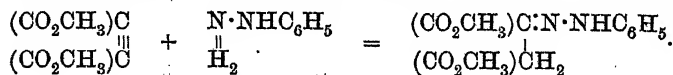
$C_{10}H_8O_3N_2$  requires  $N = 13.72$  per cent.

The colour reactions of this product coincided exactly with those mentioned above, and in fact it is identical in every respect with the acid obtained by these authors.

#### *Action of Phenylhydrazine on the Methyl Ester.*

The ester (1 mol.) was dissolved in methyl alcohol and mixed with phenylhydrazine acetate (1 mol.); the clear mixture, on standing in a desiccator over potash and sulphuric acid, soon deposited brilliant, colourless, transparent plates, which, when recrystallised from methyl alcohol, melted at 117°.

Buchner (*loc. cit.*), by the action of phenylhydrazine on methyl acetylenedicarboxylate, obtained the hydrazone of methyl oxalacetate:



The product which he obtained melted at 118°, and the properties correspond exactly with those of the compound obtained in the present instance.

#### *Oxidation of the Acid in presence of Iron.*

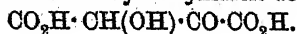
It was pointed out in the preceding communication (p. 75) that the product obtained by oxidising malic acid in presence of iron gave, with phenylhydrazine acetate, a bright orange precipitate which crystallised from hot chloroform in prisms, and melted at 217—219°. The composition of this compound does not correspond with that of a direct derivative of oxalacetic acid, but of a more oxidised product.

It appeared possible that this was the result of oxidation of a neighbouring group by the phenylhydrazine, but such does not appear to be the case, since no such substance can be obtained by the action

of excess of the reagent on pure oxalacetic acid. Probably, therefore, the oxidation is due to the hydrogen dioxide, a portion of the oxalacetic acid being further oxidised. Although only the calculated quantity of oxygen, or less, was added, it is of course possible that the product may be attacked as readily as the malic acid. In order to test this hypothesis, pure oxalacetic acid (1 mol.) was mixed with a little ferrous sulphate, and hydrogen dioxide (1 mol.) added under the conditions previously mentioned. On now adding phenylhydrazine acetate (1 mol.), an *orange* precipitate was obtained exactly similar to that originally obtained from the malic acid oxidation, which, when recrystallised from chloroform, melted at  $219^{\circ}$ . Heated with sodium carbonate solution, it gave a crystalline sodium salt, and in fact showed exact similarity in every respect.

The orange compound obtained from malic acid on different occasions was remarkably constant in composition and melting point, whereas at first sight it might be supposed, on the above explanation, that it should be mixed with variable quantities of the hydrazone of oxalacetic acid. The latter compound, however, does not begin to separate for several minutes, or in dilute solutions for over half an hour, whereas the orange compound comes down immediately; the hydrazone, moreover, cannot be recrystallised from hot solvents, and would consequently be easily separated by the treatment described.

The nature of this further oxidation product has yet to be investigated. It gives a brownish-violet colour with ferric salts in alkaline solution, and the authors are inclined to conjecture that it may be the isomeric form of dihydroxymaleic acid, namely,



#### *Oxidation of the Acid by Bromine.*

When the acid (1 mol.) is mixed with glacial acetic acid and treated with dry bromine (1 mol.), the colour of the latter quickly disappears, and, after a short time, fumes of hydrogen bromide are evolved. A similar result is obtained by using water in place of acetic acid. The product in either case, when mixed with excess of caustic soda, gives an intense *violet* with ferric chloride, exactly resembling that produced by dihydroxymaleic acid with the same reagents. The authors have reasons, however, for thinking that this product is isomeric and not identical with the latter acid, and very probably it is identical with the product obtained in the previous experiment by oxidation with hydrogen dioxide. A further study of this reaction is in progress.

From the foregoing results, it is evident that the oxidation product of maleic acid described above is free *oxalacetic acid*. Whether this

acid is to be regarded as  $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , or as the tautomeric hydroxyfumaric acid,  $\text{CO}_2\text{H}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , is, of course, a problem similar to the much discussed question of the constitution of ethyl acetoacetate. Either formula would equally well explain its formation in the present case, and the reaction with phenylhydrazine, although lending support to the ketonic formula, is of course not conclusive.

Nef (*Annalen*, 1893, 276, 230) by the hydrolysis of ethyl ethoxyfumarate, obtained an acid corresponding approximately in composition to that required for the formula  $\text{C}_4\text{H}_4\text{O}_5$ ; it melted at  $172^\circ$ , gave a dark red colour with ferric chloride, and when treated with phenylhydrazine hydrochloride, gave the phenylpyrazolonecarboxylic acid above mentioned. This acid appears to be hydroxyfumaric acid, but since it was not obtained in a pure state a strict comparison with the present acid cannot be made; the two acids may be identical or may represent the tautomeric (desmotropic) forms.

Michael and Bucher (*Ber.*, 1895, 28, 2511; 1896, 29, 1792) state that oxalacetic acid is obtained by the action of water on acetoxy-maleic anhydride, and by acting with hydrochloric acid in the cold upon ethyl oxalacetate, unsymmetrical ethyl diethoxysuccinate, &c. There are only the bare statements, however; no details, analyses, or description of the acid are given.

Many interesting reactions of the acid suggest themselves, and these the authors hope shortly to investigate.

## IX.—*Determination of the Constitution of Fatty Acids.* *Part II.*

By ARTHUR WILLIAM CROSSLEY and HENRY RONDEL LE SUEUR.

IN the first part of this research (*Trans.*, 1899, 75, 163), it was stated that among the acids then examined none contained alkyl groups in the  $\alpha$ -position, and as in such a case a new point of considerable interest is raised, we decided to prepare an acid of this type and submit it to the process there described. The acid selected was ethylisopropylacetic acid [ $\alpha$ -isopropylbutyric acid],  $\text{C}_2\text{H}_5\cdot\text{CH}(\text{C}_3\text{H}_7)\cdot\text{CO}_2\text{H}$ , which we have succeeded in preparing in large quantities from ethyl malonate. As the preparation is attended with many difficulties, we give full details of our experiments.

Ethyl cyanoacetate has recently been used in synthetical work instead of ethyl malonate, with marked success; we have also prepared ethylisopropylacetic acid from this substance as a starting point, but

the method is not to be recommended, as the yield of pure acid is not nearly so good as when ethyl malonate is employed.

Following the usual course of procedure when two alkyl groups have to be introduced into ethyl malonate, we first attempted to introduce the heavier isopropyl group and then the ethyl group, but after a long series of preliminary experiments, of which it is not necessary to give the details, we found that the yield of ethyl ethylisopropylmalonate so obtained was, relatively speaking, very small; it could, however, be increased to 75 per cent. of the theoretical by reversing the order of introduction of the alkyl groups, but even then the introduction of the isopropyl group is not an easy matter, the most satisfactory conditions being the following. After treating ethyl ethylmalonate with the calculated quantities of sodium and isopropyl iodide, the portion of the resulting liquid boiling below 230° (ethyl ethylisopropylmalonate boils at 230—235°) was again treated with sodium and isopropyl iodide (see page 90), by which means the yield of pure disubstituted ethyl malonate was increased from 46 to 75 per cent. of the theoretical.

The liquid resulting from the hydrolysis of ethyl ethylisopropylmalonate separates on distillation into two main fractions, one boiling at 202—205° (consisting of pure ethylisopropylacetic acid) and the other at about 165—175°. We were at first much puzzled to account for the presence of this liquid of lower boiling point, which had not the characteristic odour of a fatty acid, but smelt more like an ester. On consulting the literature of the subject, we found that Paal and Hoffmann (*Ber.*, 1890, 23, 1497) noticed that when diethyl isoamylmalonate is hydrolysed with alcoholic potash, there is formed, besides the corresponding malonic acid, a considerable quantity of ethyl

hydrogen isoamylmalonate,  $C_5H_{11} \cdot CH < \begin{smallmatrix} CO_2H \\ CO_2C_2H_5 \end{smallmatrix}$ , which on distillation loses carbon dioxide with production of ethyl isoamylacetate,  $C_5H_{11} \cdot CH_2 \cdot CO_2C_2H_5$ . A similar series of reactions appears to take place in the above instance; the hydrolysis of diethyl ethylisopropylmalonate gives rise to ethylisopropylmalonic acid,  $C_2H_5 \cdot C(C_3H_7)(CO_2H)_2$ , and ethyl hydrogen ethylisopropylmalonate.

On distillation, both these substances lose carbon dioxide, with the production of ethylisopropylacetic acid and its ethyl ester. The latter constitutes the fraction boiling at 165—175°, as was proved both by preparing a specimen of pure ethyl ethylisopropylacetate, which was found to boil at 164—165°, and by hydrolysing the fraction boiling at 165—175°, when it yielded pure ethylisopropylacetic acid.

We were in all cases obliged to resort to this process of double hydrolysis, for no matter whether we employed 4 or 6 mols. of potassium hydroxide, we always obtained considerable quantities of the

fraction boiling at 165—175°, even when the heating was continued for 16 hours.

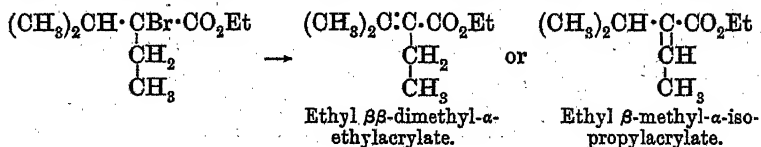
The derivatives of ethylisopropylacetic acid, prepared for the purpose of characterisation, are described in detail in the experimental part of this paper. It is interesting to note that the melting point of the amide is as high as 134°, for Burrows and Bentley (Trans., 1895, 67, 511) found that the amide of a similarly constituted and isomeric fatty acid (methylisobutylacetic acid) melted at 90°, which, as they remark, is a very low melting point for an amide of a higher fatty acid.

On comparing the physical constants and chemical properties of ethylisopropylacetic and methylisobutylacetic acids, the need of some accurate method for the determination of the constitution of such compounds is well brought out.

		Methylisobutylacetic acid, $\text{CH}_3 \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO}_2\text{H}$ .		Ethylisopropylacetic acid, $\text{C}_2\text{H}_5 \cdot \text{CH}(\text{C}_3\text{H}_7) \cdot \text{CO}_2\text{H}$ .
Acid .....	B. p.	204—205°	B. p.	202—203°
Ethyl ester.....	„	165—166	„	164—165
Chloride .....	„	152—153	„	150—153
Anilide .....	M. p.	110—111	M. p.	114—115
Amide.....	„	90	„	134—134.5
Paratoluidide...	„	86	„	122—123

It will be noticed that the boiling points or melting points of the isomeric derivatives are almost identical, except in the case of the amides and paratoluidides, two derivatives which are not, as a rule, employed for the characterisation of fatty acids, but which, in view of the above, would appear to be worth more general investigation and use.

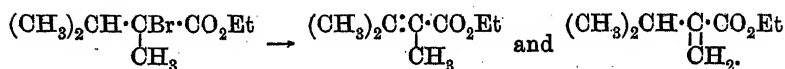
In applying our method to ethylisopropylacetic acid, we first converted it into the ethyl ester of the corresponding  $\alpha$ -bromo-acid, which was then treated with diethylaniline (see p. 95). From a glance at the formula of ethyl  $\alpha$ -bromo-ethylisopropylacetate, it is evident that the elimination of hydrogen bromide may take place in two ways :



and from oxidation experiments we conclude that both reactions occur. It appears, however, that the greater portion of the resulting unsaturated ester is ethyl  $\beta\beta$ -dimethyl- $\alpha$ -ethylacrylate, that is to say, the hydrogen atom of a CH group is more easily removed, along

with the bromine atom, than one of the hydrogen atoms of a  $\text{CH}_2$  group. Diethylaniline therefore seems to exert a certain selective action in such cases, a point on which we hope shortly to furnish more definite information.

That the course of the reaction would be twofold was to be expected from experiments which have been described by W. H. Perkin, jun. (Trans., 1896, 69, 1466, 1490), who has shown that when ethyl  $\alpha$ -bromomethylisopropylacetate is treated with quinoline or alcoholic potash a mixture of ethyl trimethylacrylate and ethyl isopropylacrylate is obtained.



Unfortunately, no definite information is given as to the amounts of the ethyl esters produced, but it is shown that ethyl trimethacrylate does not react with the sodium compound of ethyl malonate, whereas ethyl isopropylacrylate does, and calculating from the experimental data given, it would appear as if the original mixture of unsaturated ethyl salts consisted of approximately 70 per cent. of the former with 30 per cent. of the latter, thus pointing to the fact that in this case also the hydrogen atom of the  $\text{CH}$  group is the more readily eliminated.

When the mixture of acids resulting from the hydrolysis of the unsaturated ethyl esters is oxidised first with potassium permanganate and then with a mixture of potassium dichromate and dilute sulphuric acid, *acetone*, *acetic acid*, *propionic acid*, and *isobutyric acid* are obtained, as was to be expected,  $\beta\beta$ -dimethyl- $\alpha$ -ethylacrylic acid giving rise to acetone and propionic acid, and  $\beta$ -methyl- $\alpha$ -isopropylacrylic acid to acetic and isobutyric acids by rupture of the double linking.

When 25 grams of the acids were oxidised, we obtained, in separate experiments, 1.95, 1.84, and 2.07 grams of acetone. In the first two instances, the acetone was estimated by the iodoform method, and in the third by precipitation of the *p*-bromophenylhydrazone. We thought at first that by determining the amount of acetone produced we should get some idea of the proportion of the two unsaturated acids present, but from what follows it will be evident that no such information can be gathered from this experiment. Unfortunately, it is also impossible to accurately estimate the amounts of the various fatty acids produced, but acetic acid is obtained in largest quantity, propionic acid next, and but very little isobutyric acid. Had no side issues to be considered, the amount of propionic acid should be proportional to the amount of acetone, and the amount of acetic acid proportional to that of isobutyric acid, but in neither case does this hold good, there being much less acetone than would correspond to



the amount of propionic acid, and much more acetic acid than would correspond to that of isobutyric acid.

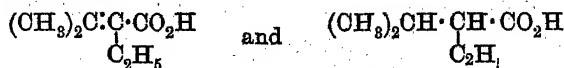
The explanation of this is not difficult to find, for we have satisfied ourselves that, under the conditions employed, both acetone and isobutyric acid are further oxidised, and thus confirm the statements of Schmidt (*Ber.*, 1874, 7, 1363) and Hercz (*Annalen*, 1877, 186, 258). Supposing, then, that acetone and isobutyric acid are formed in our experiments as primary oxidation products, they would immediately encounter an excess of oxidising agent, and consequently would both be largely converted into acetic acid, a fact which would account for the relatively large amount of this acid and for the small amounts of acetone and isobutyric acid which we find. In order to make our experiments more complete and also to supply supplementary evidence, we are at present investigating more closely the question of the oxidation of the lower fatty acids.

Applying the results of our experiments to the determination of the constitution of the acid in question, which for the moment we may presume to be of unknown structure, the argument would be as follows.

Analysis gives the molecular formula  $C_7H_{14}O_2$ , and as the acid is capable of bromination by Volhard's method, the bromine atom must occupy the  $\alpha$ -position. By eliminating this bromine atom together with a neighbouring hydrogen atom, an unsaturated substance is formed, whence it follows that, in the latter, the double bond is between the  $\alpha$ - and  $\beta$ -carbon atoms, and that the carbon atom of the CO or  $CO_2H$  group of any ketone or acid produced from this unsaturated substance by oxidation at the double bond must also have occupied either the  $\alpha$ - or  $\beta$ -position in the original acid.

In the case under investigation, we find acetone as one oxidation product, therefore the carbon atom of the ketonic group must have occupied either the  $\alpha$ - or  $\beta$ -position in the unsaturated acid. A consideration of these alternatives leads to the following results:

(1) *Occurrence in the  $\beta$ -position.*—It follows from what has just been said that the correct grouping of five of the seven carbon atoms is  $(CH_3)_2C:C\cdot CO_2H$ . Only two carbon atoms are not accounted for, and as there is but one unsatisfied bond, these must be attached as an ethyl group, so we get

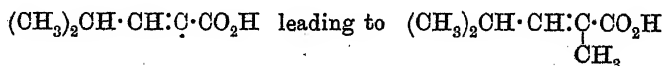


as the formulæ of the unsaturated and saturated (ethylisopropylacetic) acids. The unsaturated acid, on oxidation, would give acetone and propionic acid, both of which we have been able to identify.

(2) *Occurrence in the  $\alpha$ -position.*—We should then have the following

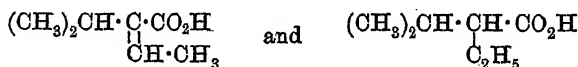
grouping,  $\text{CH}_3 > \text{C} \cdot \text{CO}_2\text{H}$ , which, as it necessitates the acceptance of a quinquivalent carbon atom, may be at once dismissed.

It might, however, be urged that all the acetone comes from the further oxidation of isobutyric acid. Then, arguing on the same lines as above, we may first place the carbon atom of the  $\text{CO}_2\text{H}$  group in isobutyric acid in the  $\beta$ -position, and obtain the following grouping for six out of the seven carbon atoms:



for the unsaturated acid: an acid which would give acetic and isobutyric acids, together with acetone from the latter on oxidation, but from which it would be impossible to obtain propionic acid.

If the carbon atom of the  $\text{CO}_2\text{H}$  group is placed in the  $\alpha$ -position, we obtain the formulæ



for the unsaturated and the saturated acids. The former would give acetic and isobutyric acids on oxidation, whilst the latter is ethylisopropylacetic acid, from which acetone and propionic acid can be obtained as already shown (p. 87).

We conclude therefore that:

(1) With an acid of the type of ethylisopropylacetic acid, our method works just as well as in the cases previously examined (*loc. cit.*).

(2) The elimination of hydrogen bromide from the ester of the corresponding bromo-acid takes place in two ways (p. 85).

(3) Acetone and propionic acid result from the oxidation of  $\beta\beta$ -dimethyl- $\alpha$ -ethylacrylic acid, and acetic and isobutyric acids from the oxidation of  $\beta$ -methyl- $\alpha$ -isopropylacrylic acid.

For the general application of this method, all fatty acids may be divided into four groups:

Group I.—Those containing two hydrogen atoms in the  $\alpha$ -position, and either one or two in the  $\beta$ -position.

The theoretical considerations connected with acids of this type have already been given (Crossley and Le Sueur, *Trans.*, 1899; 75, 161), and the process has been carried out with valeric, isovaleric, and isobutylacetic acids. In all three cases, the method works well.

Group II.—Those containing only one hydrogen atom in the  $\alpha$ -position, and either one or two in the  $\beta$ -position.

The present communication gives the theoretical considerations and a practical illustration of the method as applied to an acid of this type. Ethylisopropylacetic acid is a particularly good example, be-

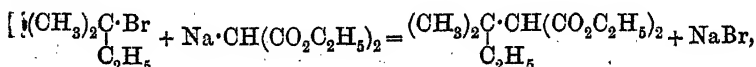
cause it contains only one  $\alpha$ -hydrogen atom, but two  $\beta$ -carbon atoms, to one of which there is attached one hydrogen atom, and to the other two hydrogen atoms.

Group III.—Those containing no hydrogen atoms in the  $\alpha$ -position.

With an acid of the constitution  $\text{CR}_3\cdot\text{CO}_2\text{H}$ , our method cannot be employed, for it is well known that, unless an acid contains an  $\alpha$ -hydrogen atom, it cannot be brominated by Volhard's method, as the molecule breaks up under these conditions (compare Reformatzky, *Ber.*, 1890, 23, 1594; Auwers and Bernhardt, *Ber.*, 1891, 24, 2210). There are, however, so few acids of this type, that, given a fatty acid incapable of being brominated by Volhard's method, without decomposition, this in itself would be strong evidence as to its constitution.

Group IV.—Those containing two hydrogen atoms in the  $\alpha$ -position and none in the  $\beta$ -position.

We cannot ascertain that an acid of this type has been described. It seems probable that such an acid should result from the product of the interaction of ethyl sodiomalonate and dimethylethylcarbonyl bromide,



but although one of us has made numerous experiments, all attempts to obtain the above condensation product have so far been without success. If, however, ethyl cyanoacetate is employed instead of ethyl malonate, a solid condensation product is produced, which is being examined in the hope that it will lead to the production of dimethylethylpropionic acid [ $\beta\beta$ -dimethylvaleric acid],  $(\text{CH}_3)_2\text{C}(\text{C}_2\text{H}_5)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

The following table shows at a glance the number of acids with from 4—7 carbon atoms occurring in each of the above four groups:

Acid.	Group I.	Group II.	Group III.	Group IV.
Butyric acids .....	1	1	—	—
Valeric acids .....	2	1	1	—
Hexoic acids .....	3	3	1	1
Heptoic acids .....	7	6	3	1

## EXPERIMENTAL.

### I. *Ethylisopropylacetic Acid.*

#### *Preparation of Ethylisopropylacetic Acid from Ethyl Ethylmalonate.*

After making a number of preliminary experiments, large quantities of ethyl ethylmalonate were worked up in the following manner. 24.8 grams of sodium (1 mol.), dissolved in 300 c.c. absolute alcohol,

were mixed with 200 grams of ethyl ethylmalonate (1 mol.), 190 grams of isopropyl iodide (1 mol.) were gradually added, and the whole heated on a water-bath for 15 hours. The greater portion of the alcohol was then distilled off, and after adding water, the whole was extracted with ether, the ethereal solution dried over calcium chloride, and the ether evaporated. After distilling the residue three times in air, using a fractionating column, the following fractions were collected :

Below 210°.....	9 grams	225—230°.....	28 grams.
210—225 .....	66 „	230—235 .....	113 „

An analysis of the fraction 230—235° gave the following numbers :

0.1182 gave 0.2712  $\text{CO}_2$  and 0.1016  $\text{H}_2\text{O}$ .  $\text{C} = 62.57$  ;  $\text{H} = 9.55$ .

$\text{C}_{13}\text{H}_{22}\text{O}_4$  requires  $\text{C} = 62.60$  ;  $\text{H} = 9.56$  per cent.

*Ethyl ethylisopropylmalonate*,  $\text{C}_2\text{H}_5 \cdot \text{C}(\text{C}_3\text{H}_7)(\text{CO}_2\text{C}_2\text{H}_5)_2$ , is a clear, colourless, mobile liquid possessing a pungent, rather unpleasant smell, and boiling at 232—233°. The yield of ester obtained is only 46 per cent. of the theoretical, but this can be materially increased by again treating the lower fractions with sodium and isopropyl iodide, in proportions calculated on the supposition that the fraction

225—230° contains 25 per cent. of unchanged ethyl ethylmalonate

210—225 „ 50 „ „ „ „

below 210 „ 100 „ „ „ „

In this way, 70 grams of liquid boiling between 230—235° were obtained, thus bringing the total yield of ethyl ethylisopropylmalonate up to 75 per cent. of that theoretically obtainable from the ethyl ethylmalonate employed.

*Ethylisopropylmalonic acid*,  $\text{C}_2\text{H}_5 \cdot \text{C}(\text{C}_3\text{H}_7)(\text{CO}_2\text{H})_2$ , was obtained by hydrolysing the ester with alcoholic potash, and after recrystallisation from benzene was analysed.

0.1670 gave 0.3370  $\text{CO}_2$  and 0.1194  $\text{H}_2\text{O}$ .  $\text{C} = 55.04$  ;  $\text{H} = 7.94$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$  ;  $\text{H} = 8.05$  per cent.

This acid is insoluble in cold light petroleum (b. p. 80—100°), readily soluble in acetone, alcohol, or water, and crystallises from benzene in beautiful, glistening needles melting at 131—131.5°. At a higher temperature, it evolves carbon dioxide, giving rise to the corresponding fatty acid.

The *silver* salt, prepared in the ordinary manner, is a white, curdy precipitate.

0.2032 gave on ignition 0.1134 Ag.  $\text{Ag} = 55.80$ .

$\text{C}_8\text{H}_{12}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 55.67$  per cent.

*Ethylisopropylacetic acid*,  $C_2H_5 \cdot CH(C_3H_7) \cdot CO_2H$ .—422 grams of ethyl ethylisopropylmalonate were heated for 10 hours on a water-bath in quantities of 100 grams at a time with 150 grams (6 mols.) of potassium hydroxide dissolved in alcohol. Water was then added, the alcohol evaporated, and after acidification with sulphuric acid the whole was extracted with ether, the ethereal solution carefully dried over calcium chloride, and the solvent evaporated. The residue, after heating to eliminate carbon dioxide, was repeatedly distilled, using a fractionating column, when the following fractions were collected :

Below $190^\circ$ .....	69.5 grams.	$196-200^\circ$ .....	12.0 grams.
$190-196$ .....	18.0 „	$200-205$ .....	128.0 „

On further distillation of the portion boiling between  $200-205^\circ$ , pure ethylisopropylacetic acid boiling constantly at  $202-203^\circ$  was obtained. It is a clear colourless, oily liquid, with a disagreeable and penetrating odour, similar to that of other acids of the fatty series. It is readily attacked by potassium permanganate in alkaline solution.

0.1466 gave 0.3476  $CO_2$  and 0.1412  $H_2O$ .  $C = 64.66$  ;  $H = 10.71$ .

$C_7H_{14}O_2$  requires  $C = 64.61$  ;  $H = 10.77$  per cent.

The *silver* salt, prepared in the usual manner, is a white caseous precipitate.

0.1988 gave on ignition 0.0902 Ag.  $Ag = 45.37$ .

$C_7H_{13}O_2Ag$  requires  $Ag = 45.57$  per cent.

We were for some time unable to account for the large fraction boiling below  $190^\circ$ , of which the major portion passes over between  $165^\circ$  and  $170^\circ$ ; further experiments showed, however, that the latter temperature is about the boiling point of ethyl ethylisopropylacetate ( $164-165^\circ$ ), and the course which the reaction is supposed to follow has already been explained in the introduction (p. 84). The whole of the liquid boiling below  $200^\circ$  was therefore again hydrolysed with alcoholic potash, when a further 60 grams of pure ethylisopropylacetic acid were obtained, thus increasing the yield to 80 per cent. of that theoretically obtainable from the corresponding disubstituted malonic ester.

#### *Preparation of Ethylisopropylacetic Acid from Ethyl $\alpha$ -Cyanoacetate.*

Ethyl  $\alpha$ -cyanoacetate was first converted into ethyl  $\alpha$ -cyanobutyrate,  $C_2H_5 \cdot CH(CN) \cdot CO_2C_2H_5$  (b. p.  $208-209^\circ$ ), by heating with sodium and ethyl iodide in alcoholic solution.

Three soda-water bottles, each containing 5 grams of sodium dissolved in 60 c.c. absolute alcohol, 31 grams of ethyl  $\alpha$ -cyanobutyrate,

and 40 grams of isopropyl iodide, were securely corked, and heated in a water-bath for 20 hours. Water was then added to the contents of the bottles, and the whole extracted with ether, &c.; the resulting liquid was then fractionated, using a column, with the following results:

Below 205° .....	11.5 grams.	220—225° .....	35.5 grams.
205—215 .....	3.5 „	225—230 .....	23.0 „
215—220 .....	10.5 „		

A nitrogen determination in the fraction 225—230° gave the following numbers:

0.1416 gave 10 c.c. moist nitrogen at 23° and 766 mm.  $N = 8.02$ .  
 $C_{10}H_{17}O_2N$  requires  $N = 7.65$  per cent.

*Ethyl  $\alpha$ -cyanoethylisopropylacetate*,  $C_2H_5 \cdot C(C_3H_7)(CN) \cdot CO_2C_2H_5$ , is a clear, colourless liquid having a faint odour of peppermint, and boils at 226—227° under 756 mm. pressure. The yield is poor (20 per cent. of the theoretical), but may be increased to 50 per cent. of the amount theoretically obtainable from the ethyl cyanobutyrate used, by again treating the lower fractions with sodium and isopropyl iodide, on the same principle as described in the preparation of ethyl ethylisopropylmalonate (p. 90).

Dilute sulphuric acid seems to be the best agent for hydrolysing this ester, but the results are not very satisfactory, and the yield of fatty acid is small.

The ester was boiled for 30 hours with four times its weight of 55 per cent. sulphuric acid, and after diluting with water the whole was extracted with ether, the ethereal solution dried over calcium chloride, and the ether evaporated. On fractionating the resulting liquid, the major portion distilled between 200° and 205°, and by repeating the process an acid liquid was obtained boiling at 202—203° and having all the properties of ethylisopropylacetic acid. It gave a white, insoluble silver salt, which was analysed:

0.1532 gave on ignition 0.0702 Ag.  $Ag = 45.82$ .  
 $C_7H_{13}O_2Ag$  requires  $Ag = 45.57$  per cent.

The *p*-toluidide crystallised from light petroleum (b. p. 60—80°) in slender, glistening, silky needles melting at 121—122° (compare p. 94).

If ethyl cyanoethylisopropylacetate is heated with dilute sulphuric acid only for 15 hours, the greater part of the resulting liquid was found to boil between 160—170°, a small amount passing over between 230° and 240°, which solidified on cooling. The fraction 160—170° consisted probably of the nitrile of ethylisopropylacetic

acid, which, from analogy, would be expected to boil at about this temperature; moreover, when heated with dilute sulphuric acid, this fraction is converted into ethylisopropylacetic acid. The solid fraction (b. p. 230—240°) crystallised from light petroleum in white, silky needles melting at 133·5—134° (see p. 94) and consisted of ethylisopropylacetamide.

0·1338 gave 12·8 c.c. moist nitrogen at 17° and 752 mm.  $N = 10·98$ .

$C_7H_{15}ON$  requires  $N = 10·85$  per cent.

In one of the first experiments we made on the hydrolysis of the above ester, a portion was heated for 12 hours with 5 times its volume of concentrated hydrochloric acid, but, as on extraction with ether, &c., the boiling point of the resulting liquid was found to be that of the original ester, the whole was heated with concentrated aqueous potassium hydroxide for 15 hours, during which process considerable quantities of ammonia were evolved. The residue extracted from the acidified liquid was found to boil for the most part below 200°, and a small portion boiling between 230° and 240° solidified on cooling. This substance crystallises from water, or, better, from light petroleum (b. p. 80—100°) in beautiful, silky needles melting at 122—122·5°, and does not sublime when heated in a dry test-tube.

0·1416 gave 13·8 c.c. moist nitrogen at 23·5° and 760 mm.  $N = 10·95$ .

$C_7H_{15}ON$  requires  $N = 10·85$  per cent.

Although resembling ethylisopropylacetamide, it melts at a temperature 13 degrees lower, and we have, so far, been unable to satisfactorily prove its exact nature, the amount obtained being very small.

#### *Derivatives of Ethylisopropylacetic Acid.*

*Ethyl ethylisopropylacetate*,  $C_2H_5 \cdot CH(C_3H_7) \cdot CO_2C_2H_5$ .—Pure ethylisopropylacetic acid was dissolved in absolute alcohol, dry hydrogen chloride passed in to saturation, and the whole left for 24 hours. After pouring into water and extracting with ether, &c., it was found that very little of the ethyl salt had been formed, as nearly the whole of the residue boiled between 200° and 205°, and consisted therefore of unchanged acid. This observation appears to be in accord with those of Menschutkin and others, who have shown that acids of this type are not readily esterified in this manner. After several further fruitless experiments, the following method was adopted.

10 grams of the pure acid were dissolved in 25 c.c. of absolute alcohol, and after adding 10 c.c. of concentrated sulphuric acid, the whole was heated on a water-bath for 8 hours; water was then added, and the oil which separated was extracted with ether. The ethereal

solution was washed with dilute sodium carbonate, then with water, carefully dried over calcium chloride, and the ether evaporated. On fractionating the residue, 11 grams (91 per cent.) of a liquid boiling constantly at 164—165° under 765 mm. pressure were obtained.

0.1486 gave 0.3708  $\text{CO}_2$  and 0.1516  $\text{H}_2\text{O}$ .  $\text{C} = 68.06$ ;  $\text{H} = 11.33$ .

$\text{C}_9\text{H}_{18}\text{O}_2$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.39$  per cent.

The ester is a clear, colourless, mobile liquid with a characteristic, penetrating smell.

*Ethylisopropylacetamide*,  $\text{C}_2\text{H}_5 \cdot \text{CH}(\text{C}_3\text{H}_7) \cdot \text{CO} \cdot \text{NH}_2$ .—The ester was heated in a sealed tube with concentrated aqueous ammonia for 12 hours at 180°, but was recovered unchanged. The same result was obtained when alcoholic ammonia was employed.

Some of the pure acid was then heated for 10 minutes in a reflux apparatus with the calculated quantity of phosphorus pentachloride. After distillation, the crude *chloride* boiling between 150° and 153° was slowly poured into concentrated aqueous ammonia, when a white solid separated, which was collected, spread on a porous plate, crystallised from light petroleum, and analysed.

0.1166 gave 11.0 c.c. moist nitrogen at 21° and 764 mm.  $\text{N} = 10.80$ .

$\text{C}_7\text{H}_{15}\text{ON}$  requires  $\text{N} = 10.85$  per cent.

The amide is but slightly soluble in chloroform, benzene, or acetone, but readily in alcohol or water, and crystallises well from either light petroleum or water in long, white, silky needles melting at 134—134.5°. When heated in a test tube, it sublimes in needle-shaped crystals.

*Ethylisopropylacetanilide*,  $\text{C}_2\text{H}_5 \cdot \text{CH}(\text{C}_3\text{H}_7) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ , prepared by heating the pure acid with twice its weight of pure aniline for 24 hours, was purified in the usual manner, and finally by recrystallisation from light petroleum (b. p. 100—120°), from which it separated in clusters of small, glistening needles melting at 114—115°. It is insoluble in water, but readily soluble in alcohol, chloroform, acetone, or ether.

0.1580 gave 9.6 c.c. moist nitrogen at 20° and 762 mm.  $\text{N} = 6.96$ .

$\text{C}_{13}\text{H}_{19}\text{ON}$  requires  $\text{N} = 6.83$  per cent.

*Ethylisopropylacetparatoluidide*,  $\text{C}_2\text{H}_5 \cdot \text{CH}(\text{C}_3\text{H}_7) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , prepared and purified in a similar way to the anilide, crystallises from light petroleum (b. p. 60—80°) in glistening, feathery needles melting at 122.5—123°. It is insoluble in water, but readily soluble in the ordinary organic solvents, even in the cold.

0.1994 gave 11.0 c.c. moist nitrogen at 19° and 762 mm.  $\text{N} = 6.36$ .

$\text{C}_{14}\text{H}_{21}\text{ON}$  requires  $\text{N} = 6.39$  per cent.



II. *Ethyl  $\alpha$ -Bromoethylisopropylacetate.*

*Ethyl  $\alpha$ -bromoethylisopropylacetate*,  $C_2H_5 \cdot CBr(C_3H_7) \cdot CO_2C_2H_5$ .—Ethylisopropylacetic acid was treated in quantities of 50 grams at a time with 4 grams of amorphous phosphorus and 120 grams of dry bromine (Volhard, *Annalen*, 1887, 242, 61). On pouring the resulting bromide into alcohol, very little heat is developed at first, but on standing the temperature gradually rises, and eventually it is necessary to moderate the reaction. The resulting ester of the bromo-acid is a colourless, mobile liquid, possessing a pungent, characteristic smell somewhat resembling that of peppermint. It boils constantly at  $135$ — $136^\circ$  under 59 mm. pressure, and is obtained in almost theoretical amount (92—93 per cent.).

0.2440 gave 0.1950 AgBr. Br = 33.97.

$C_9H_{17}O_2Br$  requires Br = 33.76 per cent.

*Treatment of Ethyl  $\alpha$ -Bromoethylisopropylacetate with Diethylaniline.*

356 grams of the ester were treated in portions of 50 grams (1 mol.) at a time with 63 grams (2 mols.) of freshly distilled diethylaniline, and worked up in the manner already described (Trans., 1899, 75, 166). As the residual liquid was found to contain traces of bromine, it was again heated with 1 mol. of diethylaniline for 8 hours, and then distilled in air. After five distillations, the following fractions were collected under 748 mm. pressure :

170—175° .....	2 grams.	185—200° .....	5 grams.
175—180 .....	170 „	Above 200 .....	28 „
180—185 .....	5 „		

The fraction boiling at  $175$ — $180^\circ$  was found to be entirely free from bromine, and gave the following numbers on analysis :

0.1094 gave 0.2774  $CO_2$  and 0.1008  $H_2O$ . C = 69.15 ; H = 10.24.

$C_9H_{16}O_2$  requires C = 69.23 ; H = 10.25 per cent.

So far this is the only instance in which we have found it possible to entirely eliminate bromine by using diethylaniline ; as a rule, the analyses of such unsaturated esters do not lead to satisfactory results, owing to the presence of small amounts of halogen.

This fraction, amounting to 73 per cent. of the product, is a clear, colourless, mobile liquid possessing a very pungent odour of peppermint ; although of fairly constant boiling point, it is not a simple substance, but as the oxidation experiments show, consists of a mixture of ethyl  $\beta\beta$ -dimethyl- $\alpha$ -ethylacrylate and ethyl  $\beta$ -methyl- $\alpha$ -isopropylacrylate.

*Hydrolysis of the Mixed Esters.*

170 grams of the mixed esters were hydrolysed in two portions with 120 grams of caustic potash dissolved in alcohol. The mixture of acids obtained from the product had the remarkable property of boiling quite constantly at  $136^{\circ}$  under 55 mm. or at  $203\text{--}204^{\circ}$  under 760 mm. pressure. It is a clear, colourless liquid, with a faint but sharp odour; it rapidly decolorises a chloroform solution of bromine, and also an alkaline solution of potassium permanganate.

*Oxidation of the mixed Unsaturated Acids.*

The mixed acids were oxidised (compare Trans., 1899, '75, 165) in quantities of 25 grams, first, with 23 grams of potassium permanganate and then with 60 grams of potassium dichromate dissolved in dilute sulphuric acid. During the second operation, an absorption apparatus was connected with the end of the condenser, in order to avoid loss of acetone. The oxidation took place very readily, in spite of the fact that the acids are insoluble in water, and was complete in from 3—4 hours. The product was distilled with steam until no more acid passed over, the distillate carefully neutralised with potassium hydroxide, again distilled with steam, and the second distillate treated with an alcoholic solution of *p*-bromophenylhydrazine, when a copious precipitate separated. This was collected and recrystallised from light petroleum, when small, glistening leaflets of the *p*-bromophenylhydrazone derivative of acetone,  $(\text{CH}_3)_2\text{C}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$ , were obtained melting at  $94\text{--}95^{\circ}$  (compare Neufeld, *Annalen*, 1888, 248, 96).

0.1212 gave 0.0994 AgBr. Br = 34.90.

$\text{C}_9\text{H}_{11}\text{N}_2\text{Br}$  requires Br = 35.24 per cent.

The contents of the distillation flask were evaporated to dryness, and the potassium salts, rendered anhydrous by heating at  $100^{\circ}$  in an air oven, were distilled with concentrated sulphuric acid, when a good deal of charring occurred. The liberated fatty acids (13—14 grams from 25 grams of the unsaturated acids) were dried by standing over concentrated sulphuric acid and then distilled fractionally, when no substance of higher boiling point than  $160^{\circ}$  was obtained.

In subsequent experiments, the process was somewhat modified, inasmuch as the potassium salts were dissolved in dilute sulphuric acid, and the whole extracted 10 times with pure ether. The ethereal solution was dried over calcium chloride, the ether removed by evaporation, and the residual fatty acids distilled, the following fractions being collected:

100—110°	125—135°	145—150°
110—125	135—145	150—160

The thermometer rises very rapidly from  $160^{\circ}$  to  $200^{\circ}$ , at about which temperature the residue passes over, and consists presumably of incompletely oxidised acids. The various fractions were further purified by drying over anhydrous sodium sulphate and repeated distillation.

*Fraction boiling at  $100-125^{\circ}$ .*—This contains acetic acid,  $\text{CH}_3\cdot\text{CO}_2\text{H}$ . A portion of this fraction boiling at  $118^{\circ}$  was converted into the silver salt, which after recrystallisation from water was analysed.

0.1288 gave on ignition 0.0834 Ag.  $\text{Ag} = 64.74$ .

$\text{C}_2\text{H}_3\text{O}_2\text{Ag}$  requires  $\text{Ag} = 64.67$  per cent.

A further quantity of the acid boiling between  $117-119^{\circ}$  was converted into the anilide, which crystallised from water in pearly scales melting at  $112-112.5^{\circ}$ .

0.1024 gave 9.2 c.c. moist nitrogen at  $20^{\circ}$  and 764 mm.  $\text{N} = 10.33$ .

$\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires  $\text{N} = 10.37$  per cent.

*Fraction boiling at  $135-145^{\circ}$ .*—This contains propionic acid,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . The silver salt, prepared from a portion of the acid boiling at  $140^{\circ}$ , gave the following numbers on analysis :

0.1520 gave on ignition 0.0908 Ag.  $\text{Ag} = 59.73$ .

$\text{C}_3\text{H}_5\text{O}_2\text{Ag}$  requires  $\text{Ag} = 59.66$  per cent.

The anilide prepared from the acid boiling between  $139-141^{\circ}$  crystallised from light petroleum in glistening leaflets melting at  $103-104^{\circ}$  (compare Trans., 1898, 73, 34).

0.1429 gave 12 c.c. moist nitrogen at  $20^{\circ}$  and 753 mm.  $\text{N} = 9.51$ .

$\text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires  $\text{N} = 9.39$  per cent.

*Fraction boiling at  $150-160^{\circ}$ .*—This contains isobutyric acid  $(\text{CH}_3)_2\text{CH}\cdot\text{CO}_2\text{H}$ . The portion of this *small* fraction boiling between  $153^{\circ}$  and  $157^{\circ}$  was converted into the calcium salt by heating the acid dissolved in water with pure calcium carbonate, filtering, and evaporating the filtrate in a vacuum, when radiating clusters of silky needles were obtained, in which, after drying in air, the water of crystallisation was determined.

0.3536 lost 0.0702 at  $155^{\circ}$ .  $\text{H}_2\text{O} = 19.85$ .

0.2368 gave 0.1536  $\text{CaSO}_4$ .  $\text{Ca} = 19.07$ .

$(\text{C}_4\text{H}_9\text{O}_2)_2\text{Ca}$  requires  $\text{Ca} = 18.69$  per cent.

According to Chancel and Parmentier (*Compt. rend.*, 1887, 104, 477), calcium isobutyrate should contain  $5\text{H}_2\text{O}$ , requiring 29.6 per cent.  $\text{H}_2\text{O}$ , but, as has repeatedly been shown (Trans., 1898, 73, 15, 35; also 1899, 75, 185), the salt prepared in the above manner contains

water corresponding more nearly with  $4\text{H}_2\text{O}$  (25·17 per cent.), the amount depending to a large extent on the length of time during which the salt has been exposed to air (Trans., 1898, 73, 15).

The unusually small proportion of water found above appears to be due to the facts that, first, as the calcium analysis shows, the salt was not quite pure, and, secondly, when the solution of the salt was evaporated sufficiently for it to crystallise, the surface became coated with a crust, from which, on account of the small amount of material, it was very difficult to completely detach the crystals.

As mentioned on p. 95, when ethyl  $\alpha$ -bromoethylisopropylacetate is treated with diethylaniline, 28 grams of a substance boiling above  $200^\circ$  were obtained, besides the unsaturated esters. On distilling this under 65 mm. pressure, 8 grams were found to boil below  $200^\circ$ , and 14 grams between  $205$ — $210^\circ$ . As both fractions contained nitrogen, it was thought that an ethyl ester of an anilino-acid might have been produced, for, as Bischoff (*Ber.*, 1898, 31, 3015) has shown, these substances are formed by the action of dimethylaniline on the ethyl esters of  $\alpha$ -bromo-acids of the fatty series, but it appears not to be so in this case.

The *fraction boiling below  $200^\circ$*  was treated with alcoholic potash, the alcohol evaporated, and a small amount of an insoluble nitrogenous substance removed by ether. On acidifying and extracting with ether, 7 grams of a liquid boiling between  $207$ — $209^\circ$  were obtained, which exhibited all the properties of the mixture of unsaturated acids described on p. 96. A portion was converted into the silver salt and analysed.

0·1708 gave, on ignition, 0·0788 Ag. Ag = 46·13.

$\text{C}_7\text{H}_{11}\text{O}_2\text{Ag}$  requires Ag = 45·96 per cent.

The *fraction boiling at  $205$ — $210^\circ$*  was again distilled, and a portion boiling at  $207$ — $208^\circ$  under 60 mm. pressure was analysed :

0·1558 gave 0·4264  $\text{CO}_2$  and 0·1288  $\text{H}_2\text{O}$ . C = 74·64 ; H = 9·18.

0·2261 „ 13·6 c.c. moist nitrogen at  $16^\circ$  and 766 mm. N = 7·06.

0·2090 „ 11·9 c.c. „ „ „  $15^\circ$  „ 770 mm. N = 6·76.

$\text{C}_{17}\text{H}_{27}\text{O}_2\text{N}$  requires C = 73·64 ; H = 9·71 ; N = 5·05 per cent.

These numbers do not agree with those required for the ethyl ester of the corresponding anilino-acid. Some of the liquid was then heated with excess of alcoholic potash for 7 hours. Water was added and the alcohol evaporated, when on extracting the alkaline liquid with ether, nearly the total weight of liquid originally taken was obtained. It boils constantly at  $290$ — $295^\circ$  under 750 mm. pressure, is a thick, pale yellow liquid with a marked blue fluorescence, and gave C = 76·52,

H = 8.99, N = 7.31 per cent. as the mean of three closely agreeing analyses. It dissolves in concentrated sulphuric or hydrochloric acids, but is thrown out of solution on adding water. With concentrated sulphuric acid and a crystal of potassium dichromate, it gives a rose-pink colour turning to greenish-brown. Concentrated nitric acid dissolves it, and on evaporation a rose-pink colour is developed. Potassium permanganate is readily decolorised by it, but no definite oxidation product could be isolated, and we have so far been unable to decide the nature of this substance.

Our thanks are due to the Research Fund Committee of the Chemical Society for a grant defraying in part the cost of the materials used in this investigation.

CHEMICAL LABORATORY,  
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### X.—*Preparation of Benzeneazo-o-nitrophenol.*

By J. T. HEWITT.

BENZENEAZO-O-NITROPHENOL being required for some work on which the author of the present communication is engaged, an attempt was made to prepare it in a more satisfactory manner than according to Noelting's process, which consists in adding a solution of a phenyl-diazonium salt to an alkaline solution of *o*-nitrophenol (*Ber.*, 1887, 20, 2997). Diazotised amines combine but slowly with *o*-nitrophenol, and during the process considerable decomposition sets in, the yield being small. Direct nitration of benzeneazophenol gave *p*-nitrobenzeneazophenol (Noelting, *loc. cit.*), the method consisting in carrying out the nitration in a strong sulphuric acid solution.

It seemed possible, however, by altering the conditions of the experiment, that substitution might take place in the phenol nucleus, and that if so, the desired *o*-nitro-compound would be obtained, as it was very improbable that the nitro-group should enter in the meta-position, whilst the para-position is already occupied by the azo-group. The desired result was obtained, the necessary conditions being that the nitric acid is sufficiently dilute and the temperature carefully regulated.\*

\* E. Täuber (*Ber.*, 1893, 26, 1872) has described the nitration of phenolazo-benzenesulphonic acid in strong sulphuric acid, and obtained a nitro-derivative

10 grams of benzeneazophenol (powdered) are stirred up and thoroughly moistened with a cold mixture of 20 c.c. nitric acid of sp. gr. 1.36 and 60 c.c. water. The mixture is then carefully warmed on the water-bath, the temperature being gradually raised to about  $40^{\circ}$  (the temperature of the water-bath should not be above  $45^{\circ}$ ). After about 20 minutes, a smell resembling that of *o*-nitrophenol is noticeable, the mass becomes thicker, and eventually bubbles of gas make their appearance. At this stage, when the contents of the beaker have become a stiff paste, in which the thermometer will stand upright, they are added to an excess of cold water, and the insoluble part collected rapidly with the aid of a pump and well washed. After drying at  $100^{\circ}$ , the weight of yellow precipitate is generally  $7\frac{1}{2}$  grams, and the melting point about  $122^{\circ}$  (not quite sharp).

Noelting gives  $126^{\circ}$  as the melting point of benzeneazo-*o*-nitrophenol; after three recrystallisations from benzene, the melting point of the above product was found to be constant at  $126.5^{\circ}$  ( $128.5^{\circ}$  corrected; the remaining melting points in this paper are all corrected for the apparent expansion of the mercury of the thermometer). The composition of the substance was controlled by an analysis.

0.1200 gave 0.2572  $\text{CO}_2$  and 0.0390  $\text{H}_2\text{O}$ . C = 58.46; H = 3.61.

0.1377 ,, 21.0 c.c. moist nitrogen at  $16^{\circ}$  and 762 mm. N = 17.76.

$\text{C}_{12}\text{H}_9\text{O}_3\text{N}_3$  requires C = 59.21; H = 3.73; N = 17.32 per cent.

If considerable quantities are desired, benzeneazophenol may be nitrated in much greater amount than 10 grams at a time, and after checking its melting point, the product can be used for most purposes without recrystallisation.

As benzeneazo-*o*-nitrophenol could be obtained in considerable quantities, it was considered desirable to characterise the compound more closely than had hitherto been done. The substance crystallises in small light yellow needles, gives a pale yellow powder, and forms yellow solutions in organic solvents. In strong sulphuric acid, it dissolves with a red colour, and the careful addition of water to the solution at first precipitates a red sulphate which, however, very readily gives the yellow nitrophenol on further addition of water. Whether the precipitate so obtained is a hydrate or the free azophenol, has not so far been determined. Farmer and Hantzsch state in a recent paper (*Ber.*, 1899, 32, 3098) that this azophenol (or,

with the nitro-group in the ortho-position relatively to the hydroxyl. He expressly mentions in his paper that he has chosen such a sulphonic acid derivative, as otherwise the nitro-group would enter the benzene, and not the phenol, nucleus. The course of the substitution really depends on whether an azophenol reacts as such, or as a salt of a mineral acid.

in their nomenclature, *Nitrochinon-Phenylhydrazon*) gives neither hydrate nor hydrochloride. The existence of the sulphate shows, however, that the azophenol is capable of forming salts with strong acids.

Solutions of the azophenol in fixed alkalis and ammonia are of a distinct red shade, in fact, the difference of colour between the free phenol and its alkaline salts strongly recalls the relationship in colour between *o*-nitrophenol and its alkali salts. The sodium salt separates in red needles on concentration, and in neutral solution gives, with solutions of metallic salts, the following precipitates.

*Silver Nitrate*.—Light orange precipitate, practically insoluble, even in boiling water.

*Magnesium Chloride*.—Orange precipitate, dissolves somewhat in boiling water, and separates in groups of small needles on cooling.

*Zinc Sulphate*.—Bright yellow precipitate, becoming crystalline on warming, slightly soluble in boiling water.

*Cadmium Sulphate*.—Orange precipitate, very slightly soluble.

*Mercuric Chloride*.—Yellow precipitate, appreciably soluble in boiling water.

*Calcium Chloride*.—Orange red precipitate, very slightly soluble in boiling water.

*Strontium Chloride*.—Similar precipitate to that with calcium chloride, but somewhat redder in shade.

*Barium Chloride*.—Scarlet precipitate, very sparingly soluble in boiling water, from which it separates in very slender, long needles.

*Lead Acetate*.—Orange precipitate, insoluble.

*Copper Sulphate*.—Dirty orange precipitate, insoluble.

*Cobalt Nitrate* or *Nickel Chloride*.—Reddish-brown precipitate.

*Manganese Sulphate*.—Orange precipitate, somewhat soluble in boiling water.

*Stannous Chloride*.—Bright sulphur-yellow precipitate.

*Ferrous Sulphate*.—Dark brown precipitate, soon turning green.

*Ferric Chloride*.—Bright sulphur-yellow precipitate.

*Aluminium Sulphate*.—Bright yellow precipitate.

*Chrome Alum*.—Yellow precipitate, not quite so clear in shade as that with aluminium.

It is somewhat striking that the colours of the precipitates should vary so much. The very slight solubility of the barium salt contrasts strongly with that of the barium salts of benzeneazophenols containing the substituents in the benzene nucleus, which may be recrystallised easily from boiling water and are obtained as orange needles containing  $4\text{H}_2\text{O}$ .

The *acetyl* derivative,  $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ , is easily

obtained by warming 2 parts of the azophenol, 2 parts of fused powdered sodium acetate, and 5 parts of acetic anhydride for 1 hour on the water-bath. It separates in a flocculent state on pouring into water, and may be obtained as yellowish-brown prisms by recrystallisation from glacial acetic acid or benzene. It melts at  $120.5^{\circ}$ .

0.1237 gave 0.2644  $\text{CO}_2$  and 0.0428  $\text{H}_2\text{O}$ .  $\text{C} = 58.29$ ;  $\text{H} = 3.85$ .

0.1103 „ 14.5 c.c. moist nitrogen at  $21^{\circ}$  and 756 mm.  $\text{N} = 14.89$ .

$\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}_3$  requires  $\text{C} = 58.90$ ;  $\text{H} = 3.89$ ;  $\text{N} = 14.77$  per cent.

The acetyl derivative is easily soluble in acetone, ethyl acetate, or pyridine, less so in chloroform or benzene; methylated spirit dissolves it sparingly in the cold, but fairly readily on warming, as does amyl alcohol. It is sparingly soluble in ether and insoluble in light petroleum.

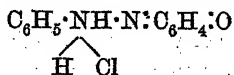
The *benzoyl* derivative,  $\text{C}_6\text{H}_5 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_5(\text{NO}_2) \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , is obtained when equal weights of the azophenol and benzoyl chloride are boiled gently for 1 hour. After pouring the product into water and leaving it until it has solidified, it is powdered, warmed with a little alcohol, and washed with repeated small quantities of cold alcohol on the pump. It separates from benzene in small, yellow crystals, melts at  $132^{\circ}$ , is easily soluble in hot benzene, acetone, or chloroform, sparingly so in alcohol or light petroleum, and is only dissolved in very small quantities by ether.

0.1127 gave 12.4 c.c. moist nitrogen at  $13^{\circ}$  and 764 mm.  $\text{N} = 13.07$ .

$\text{C}_{19}\text{H}_{13}\text{O}_4\text{N}_3$  requires  $\text{N} = 12.72$  per cent.

The difference in the behaviour of benzeneazophenol on nitration, when the operation is effected with dilute acid or in concentrated sulphuric acid solution, might be explained if benzeneazophenol had the constitution,  $\text{C}_6\text{H}_5 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , usually assigned to it.

Phenols undergo substitution much more readily than benzene derivatives, in which no hydroxyl or amino-groups are present, and hence nitration might be expected to occur in the phenol nucleus. On the other hand, when nitration takes place in a sulphonic acid solution, a salt of the azophenol with a mineral acid is being nitrated, and if to these salts a formula is assigned, such as that which Hantzsch (*Ber.*, 1899, 32, 3091) gives to the hydrochloride,



the result is also easily explicable. Quinones are substituted with comparative difficulty, amines, on the contrary, with ease, an ortho- or a para-derivative being produced. Hantzsch, however, assigns a similar



quinonoid structure to the free azophenols, and this seems to be hardly reconcilable with the experiments just described. It may be pointed out that the colour of the free azophenols much more closely corresponds to that of their ethers and esters, which undoubtedly possess the azo-structure, than to that of their salts with mineral acids for which the structure of quinone-hydrazone derivatives is probable.

The author desires to thank Messrs. Clacher and Likiernik for help afforded in this work.

EAST LONDON TECHNICAL COLLEGE.

# XI.—*Ethyl Dibromobutanetetracarboxylate and the Synthesis of Tetrahydrofurfuran-2:5-dicarboxylic Acid.*

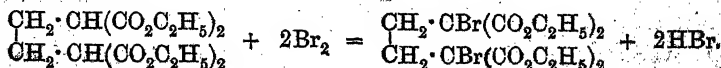
By BEVAN LEAN, D.Sc., B.A.

In a paper communicated to the Society a few years ago (Trans., 1894, 65, 995), the author described a number of homologues of butanetetracarboxylic acid and of adipic acid. It was shown that ethyl butanetetracarboxylate, when treated with sodium ethoxide and alkyl haloids, yields disubstitution derivatives of the general formula  $(\text{CO}_2\text{C}_2\text{H}_5)_2\text{RC}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CR}(\text{CO}_2\text{C}_2\text{H}_5)_2$ .

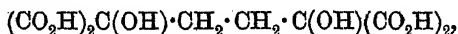
From these, symmetrical dialkyl butanetetracarboxylic acids and dialkyl adipic acids were obtained, and it was shown that the latter always existed in two modifications, usually differing from one another markedly in melting point, solubility, and other physical properties.

At the time that this communication was made, it had also been found that bromine could readily replace the hydrogen atoms of the two CH groups in ethyl butanetetracarboxylate, and that the two bromine atoms of the resulting compound could, in turn, be replaced by hydroxyl groups on digestion with barium hydroxide. The investigation of dihydroxybutanetetracarboxylic acid and of its derivatives proved, however, to be a matter of much greater difficulty and interest than was anticipated, and it now appears desirable to no longer postpone the communication of the results of this part of the inquiry.

Ethyl butanetetracarboxylate, like ethyl pentanetetracarboxylate (Perkin, Trans., 1891, 59, 827), readily reacts, in chloroform solution, with bromine with the formation of ethyl  $\alpha\delta$ -dibromobutanetetracarboxylate and evolution of hydrogen bromide, thus:

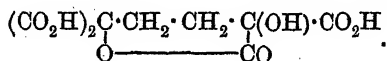


The beautiful, crystalline dibromo-compound thus obtained, when digested for some hours with a strong solution of barium hydroxide, yields an insoluble barium salt of dihydroxybutanetetracarboxylic acid, crystallising apparently with one molecular proportion of water. When this salt is decomposed by sulphuric acid, dihydroxybutanetetracarboxylic acid,



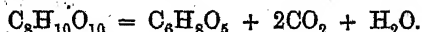
is obtained in solution, as is shown by the preparation and analysis of its silver salt, which has the composition  $\text{C}_8\text{H}_6\text{O}_{10}\text{Ag}_4$ .

On slowly concentrating the aqueous solution of dihydroxybutanetetracarboxylic acid over strong sulphuric acid, beautiful, long, prismatic needles are obtained of the corresponding  $\delta$ -monolactone,

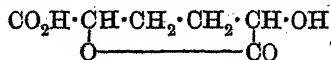


The silver salt prepared from this substance is silver dihydroxybutanetetracarboxylate,  $\text{C}_8\text{H}_6\text{O}_{10}\text{Ag}_4$ , thus confirming this view of its constitution.

On heating an aqueous solution of this  $\delta$ -lactone in a sealed tube at  $150^\circ$ , decomposition ensues with the elimination of carbon dioxide. If the aqueous solution of the product is evaporated to a small bulk on a water-bath and placed over sulphuric acid in a vacuum, small, star-shaped clusters of crystals appear after one or two days; if left longer over sulphuric acid, the whole eventually becomes solid, but the last traces of moisture disappear very slowly. The product had the composition  $\text{C}_6\text{H}_8\text{O}_5$ , which is that of dihydroxyadipic acid, less 1 molecular proportion of water,



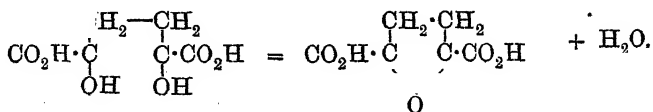
In this case, again, the simplest explanation would be that the substance is the  $\delta$ -lactone of dihydroxyadipic acid, namely,



Careful investigation, however, has shown that the silver salt prepared from it has the composition  $\text{C}_6\text{H}_6\text{O}_5\text{Ag}_2$ , rendering it very improbable that the substance  $\text{C}_6\text{H}_8\text{O}_5$  is a  $\delta$ -lactone: for this to be the case, it would be necessary to suppose the lactonic ring to be quite exceptionally stable, remaining intact when the substance is dissolved in water, and also to assume that the hydrogen atom of the hydroxyl group has an acidic character—a very unusual occurrence in an aliphatic compound.

Further consideration shows, however, that the elimination of water

actually takes place between the two hydroxyl groups, and that the substance is tetrahydrofurfuran-2:5-dicarboxylic acid, formed in the following way:



It was found that the tetrahydrofurfurandicarboxylic acid ( $\text{C}_6\text{H}_8\text{O}_5$ ) obtained by heating an aqueous solution of dihydroxybutanetetracarboxylic acid begins to melt about  $65^\circ$ , but on raising the temperature the fusion proceeds only gradually, and is not complete until about  $120^\circ$ . The absence of a definite melting point suggested the possibility of the substance being a mixture of stereoisomeric acids, and experiments were instituted to separate them if possible by fractional crystallisation from water.

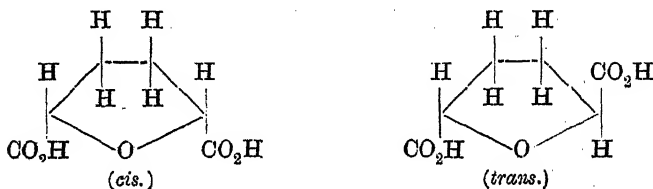
Using 32 grams of material, there was little difficulty in separating 6 grams of a tetrahydrofurfurandicarboxylic acid which melted at  $123-125^\circ$ . This was shown to be dibasic by the preparation and analysis of its silver salt, which was found to have the composition  $\text{C}_6\text{H}_6\text{O}_5\text{Ag}_2$ . It is to be noted that it crystallised fairly readily from a little water in star-shaped clusters, and that it was not necessary to dry the crystals over strong sulphuric acid for analysis, exposure in the air being sufficient. It appeared to have no tendency to combine with a molecular proportion of water, as would be the case with a  $\delta$ -lactone, for an aqueous solution, after being boiled, gave again the silver salt mentioned above, and not a salt of the formula  $\text{C}_6\text{H}_8\text{O}_5\text{Ag}_2$ .

The mother liquor from which this acid had been separated was carefully examined, as is described later (p. 113), and from it were isolated 8 grams of small, white crystals, which when dried in the air melted at  $56.5-62^\circ$ . It was at first expected that this substance was a second tetrahydrofurfurandicarboxylic acid; analysis, however, proved it to have the composition  $\text{C}_6\text{H}_8\text{O}_5 + \text{H}_2\text{O}$  or  $\text{C}_6\text{H}_{10}\text{O}_6$ . The silver salt prepared from it had the composition  $\text{C}_6\text{H}_6\text{Ag}_2\text{O}_6$ , a result which led to the conclusion that the substance  $\text{C}_6\text{H}_{10}\text{O}_6$  was not dihydroxyadipic acid, but the isomeric monohydrate of tetrahydrofurfurandicarboxylic acid. The only solvent from which it was found at all feasible to crystallise this substance was strong hydrochloric acid; it then melted at  $63-64^\circ$ , and analysis proved it to be unchanged in composition.

When placed a few hours over strong sulphuric acid, it was found that the monohydrate,  $\text{C}_6\text{H}_{10}\text{O}_6$ , could no longer be fused below  $70^\circ$ , and after 8 days the product melted at  $93-95^\circ$  and had the composition  $\text{C}_6\text{H}_8\text{O}_5$ . Its silver salt was found to have the composition  $\text{C}_6\text{H}_6\text{O}_5\text{Ag}_2$ , confirming the conclusion that the substance was a tetrahydrofurfuran-

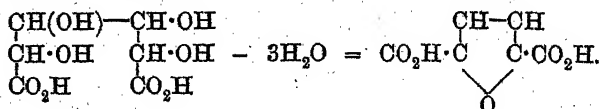
dicarboxylic acid, and not the isomeric  $\delta$ -monolactone of dihydroxyadipic acid. When this acid (m. p.  $93-94^\circ$ ) was exposed in the air or dissolved in a little water and the solution evaporated over solid potassium hydroxide, the product melted at  $57-62^\circ$ , the monohydrate having been reformed.

In the previous paragraphs it has been shown that if an aqueous solution of dihydroxybutanetetracarboxylic acid is heated in a sealed tube at  $150^\circ$ , the product must be regarded as a mixture of isomeric tetrahydrofurfurandicarboxylic acids, the one melting at  $123-125^\circ$ , the other at about  $93-94^\circ$ . The isomerism of these must be geometric; they are, in fact, *cis*- and *trans*-forms, recalling the isomeric hexahydrotetraphthalic acids, and may be represented thus:



So far as is known, this is the first case of geometrical isomerism which has been established in the furfuran series.

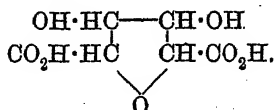
Few instances are recorded of the formation of a furfuran derivative by the removal of the elements of water from an open chain hydroxylic compound. Fischer (*Ber.*, 1891, 24, 2140) has shown that water can be split off from the tetrahydroxyadipic acids, with the formation of a furfurandicarboxylic acid (dehydromucic acid), thus:



This action, however, is not strictly analogous to the case discussed in the present paper, because water was eliminated only when the hydroxyadipic acids were heated with strong acids.

Another instance which is more nearly parallel seems to exist in the case of Tiemann's 'isosaccharic acid' (*Ber.*, 1884, 17, 247; 1886, 19, 1257). This was at first regarded as a tetrahydroxyadipic acid,  $\text{C}_6\text{H}_{10}\text{O}_8$ , but more recently (*Ber.*, 1894, 27, 118) was shown to have the composition  $\text{C}_6\text{H}_8\text{O}_7$ . Tiemann gave the name 'nor-isosaccharic acid' to the tetrahydroxyadipic acid from which 'isosaccharic acid' might be considered to be derived, and pointed out that on the analogy of saccharic and mucic acids, the substance  $\text{C}_6\text{H}_8\text{O}_7$  might be regarded as the lactone of this acid but for the facts that it proved to be dibasic, and

that when heated alone, or in a stream of dry hydrogen chloride, it was changed, without charring, into pyromucic acid. He therefore concluded that 'isosaccharic acid' was really 3:4-dihydroxytetrahydrofurfuran-2:5-dicarboxylic acid,

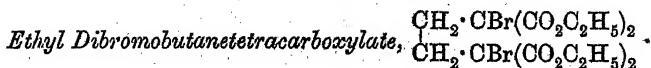


Of the various compounds prepared from this substance, Tiemann found that several were derivatives of what he continued to term 'isosaccharic acid,' but that others contained, in addition, the elements of one molecular proportion of water. The latter, he pointed out, might be regarded as furfuran derivatives crystallised with  $1\text{H}_2\text{O}$ , but, as other dihydroxyfurfurans were not known, and as a tetrahydroxyadipic acid, which lost water when its aqueous solution was evaporated, might be expected to undergo hydration under the influence of chemical agents, he continued to speak of them as formed from 'nor-isosaccharic acid.' In confirmation of this view, he described a tetracetyl derivative of 'nor-isosaccharic acid' (*Ber.*, 1894, 27, 128), but it is not stated how this was isolated, nor are any analyses quoted.

It may be noted that some of the derivatives of 'nor-isosaccharic acid' were found to lose readily one molecular proportion of water, giving rise to corresponding derivatives of 'isosaccharic acid,' and that the latter readily recombined with water in molecular proportion. A number of salts of 'nor-isosaccharic acid' were described, but almost all of these contained water of crystallisation, and it is not clear how Tiemann satisfied himself that they were not derived from 'isosaccharic acid.'

From a review of these facts, it appears to the author of the present paper that the compounds described by Tiemann as derivatives of 'isosaccharic acid,' or of 'nor-isosaccharic acid,' are in reality derivatives of 3:4-dihydroxytetrahydrofurfuran-2:5-dicarboxylic acid, and that the names 'isosaccharic acid' and 'nor-isosaccharic acid' should be abandoned.

#### EXPERIMENTAL.



80 grams of ethyl butanetetracarboxylate, free from ethyl butanetricarboxylate (compare Lean and Lees, *Trans.*, 1897, 73, 1062), were dissolved in 230 grams of chloroform in a flask connected with a reflux condenser, and 73 grams of dry bromine run in drop by drop, the flask

being kept cool during the operation. The liquid remained colourless until nearly the whole of the bromine had been added; the flask was then warmed at 50° for 5 hours on the water-bath, and finally for 1 hour at 70°.

The product, which was still coloured by bromine, was shaken with a small quantity of a solution of sodium hydrogen sulphite, and the residual heavy, yellowish oil washed with water and dehydrated by calcium chloride. After the chloroform had been removed as far as possible by evaporation on the water-bath, the residue, on standing, solidified almost completely, forming a beautiful, crystalline mass (about 108 grams). This was broken up and separated as completely as possible from oil by washing with a little ethyl alcohol with the aid of a pump. The white, crystalline product (87 grams) was further freed from traces of oil by dissolving it in the least possible quantity of hot ethyl alcohol, when the solution deposited, on standing, about 76 grams of colourless, monoclinic prisms. If crystallised again from alcohol, almost exactly the same weight (75 grams) was recovered. On analysis:

0.1517 gave 0.2127 CO<sub>2</sub> and 0.0680 H<sub>2</sub>O. C = 38.33; H = 4.98.

0.1639 „ 0.1283 AgBr. Br = 32.01.

0.2385 „ 0.1775 AgBr. Br = 31.67.

C<sub>16</sub>H<sub>24</sub>O<sub>8</sub>Br<sub>2</sub> requires C = 38.09; H = 4.76; Br = 31.74 per cent.

Ethyl dibromobutanetetracarboxylate crystallises in well-formed, monoclinic crystals from a warm solution in light petroleum, or in methyl or ethyl alcohol, melts at 83°, and is readily soluble in ether, benzene, toluene, or glacial acetic acid.

*Dihydroxybutanetetracarboxylic Acid*,  $\begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{OH})(\text{CO}_2\text{H})_2 \\ \text{CH}_2 \cdot \text{C}(\text{OH})(\text{CO}_2\text{H})_2 \end{array}$

When ethyl dibromobutanetetracarboxylate is hydrolysed in a glass flask, a considerable quantity of silica and alkali is introduced into solution, from which it is very difficult to free the product, no solvent besides water having been found from which dihydroxybutanetetracarboxylic acid can be crystallised; the hydrolysis therefore was carried out in a silver flask of 750 c.c. capacity.

80 grams of ethyl dibromobutanetetracarboxylate (1 mol.) along with 157 grams of barium hydroxide (2 mols.) freshly crystallised in a platinum basin, and about 300 c.c. of water were introduced into the silver flask, to the neck of which a small reflux condenser was attached. The mixture was then boiled on a sand-bath for 6 hours. A further quantity of barium hydroxide (157 grams) was then added, and the heating continued for another 6 hours. The product, while still hot, was filtered with the aid of a pump, and the insoluble, white, crystalline

barium dihydroxybutanetetracarboxylate was washed many times with hot water, then suspended in water, and decomposed with the necessary amount of sulphuric acid. After filtration from barium sulphate, the solution was always found to contain a small quantity of bromine; to remove this, silver hydroxide was added, and, lastly, the excess of silver was removed by sulphuretted hydrogen. The filtered solution was then evaporated to about 150 c.c. on the water bath.

*Silver Salt.*—A portion of the solution was neutralised with ammonium hydroxide solution, poured into a large excess of silver nitrate solution, and the mixture well shaken; the white, amorphous precipitate was collected on a filter, well washed with water and dried on a porous plate, and finally over sulphuric acid.

0.2910 gave 0.1820 AgBr.  $\text{Ag} = 62.54$ .

$\text{C}_3\text{H}_6\text{O}_{10}\text{Ag}_4$  requires  $\text{Ag} = 62.23$  per cent.

*Barium Salt.*—Some of the barium salt formed in preparing the acid was washed many times with boiling water, and afterwards dried on a porous tile and by exposure on a watch glass in the air for some days.

0.6248 gave 0.5218  $\text{BaSO}_4$ .  $\text{Ba} = 49.12$ .

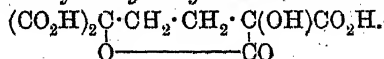
$\text{C}_3\text{H}_6\text{O}_{10}\text{Ba}_2 + \text{H}_2\text{O}$  requires  $\text{Ba} = 49.50$  per cent.

This salt apparently crystallises with  $1\text{H}_2\text{O}$ , but the water cannot be estimated by desiccation at  $110^\circ$ , as further decomposition ensues.

A strong solution of dihydroxybutanetetracarboxylic acid has an extremely acid taste, whilst a dilute solution has a taste very similar to that of alum. The acid readily liberates carbon dioxide from a carbonate.

When the aqueous solution of the acid was concentrated over sulphuric acid in a vacuum, a deposit of barium sulphate formed before crystallisation began. On further evaporation, a little more barium sulphate separated out, and shortly afterwards beautiful, long, prismatic needles of the monolactone of dihydroxybutanetetracarboxylic acid began to separate from the slightly yellow, gelatinous mass.

*$\delta$ -Monolactone of Dihydroxybutanetetracarboxylic Acid,*



The gelatinous product, in which crystals had begun to form, was stirred up and after exposure for some days in a vacuum over sulphuric acid became solid and dry. The hard, white, porcelain-like mass was powdered and again exposed over sulphuric acid. The yield from 80 grams of ethyl dibromobutanetetracarboxylate was usually 30—35 grams. The substance began to soften at  $145^\circ$ , and at  $156^\circ$  it was

completely fused and frothed up the capillary tube. At a higher temperature, it charred rapidly.

On igniting 1.0966 grams of the substance, 0.0056 gram or 0.5 per cent. of ash was left, which proved to be mainly barium sulphate. In the following analyses, a correction of 0.5 per cent. was made upon the weight of substance taken. No solvent, besides water, was found from which the acid could be crystallised.

0.1548 gave 0.2168  $\text{CO}_2$  and 0.0505  $\text{H}_2\text{O}$ . C = 38.24; H = 3.65.

0.1616 „ 0.2304  $\text{CO}_2$  „ 0.0523  $\text{H}_2\text{O}$ . C = 38.86; H = 3.61.

$\text{C}_8\text{H}_{10}\text{O}_{10}$  requires C = 36.06; H = 3.78 per cent.

$\text{C}_8\text{H}_8\text{O}_9$  „ C = 38.68; H = 3.25 „

These analyses showed that the substance consisted probably of the  $\delta$ -monolactone of dihydroxybutanetetracarboxylic acid: it was proved to be a lactone, and not a furfuran derivative, by analysis of the silver salt.

The *silver salt* was prepared, and proved to be tetrabasic.

0.3410 gave 0.3697 AgBr. Ag = 62.27.

0.245 „ 0.2662 AgBr. Ag = 62.41.

$\text{C}_8\text{H}_6\text{O}_{10}\text{Ag}_4$  requires Ag = 62.23 per cent.

The lactone of dihydroxybutanetetracarboxylic acid crystallises in long needles on slow evaporation of its aqueous solution. It is readily soluble in water, ether, methyl, or ethyl alcohol, but insoluble in benzene, toluene, or light petroleum. On exposure in the air, it absorbs moisture, but only very slowly.

### *Tetrahydrofurfuran-2:5-dicarboxylic Acid.*

On heating an aqueous solution of the lactone of dihydroxybutanetetracarboxylic acid in a sealed glass tube, the acid decomposed with the elimination of carbon dioxide.

About 2 grams of the lactone of dihydroxybutanetetracarboxylic acid, dissolved in 20 c.c. of water, were heated at  $150^\circ$  in a sealed tube for 6 hours. A very considerable pressure was developed within the tube, so much so that until a special quality of Jena glass tubing was obtained, almost every tube was shattered, and much valuable material lost. On opening the tube, a violent escape of carbon dioxide took place, and the decomposition was found to be complete. Fifty-six grams of the lactone were successfully decomposed, and the contents of the tubes were mixed and filtered from a little sediment.

A portion was examined as follows: 120 c.c. were evaporated to a small bulk on a water-bath and placed over sulphuric acid in a vacuum; in the course of the next night, a small sediment separated out, which proved to be barium sulphate (compare p. 109); this was



removed by filtration and the slow evaporation continued. In the course of another day, small, star-shaped forms resembling snow-crystals began to appear, and after four more days almost the whole became solid. The cake was then broken up and placed for a fortnight over sulphuric acid in a vacuum; the last traces of moisture seemed to disappear very slowly.

On ignition, a small amount of mineral matter was left; 0.5327 gram gave 0.0068 gram or 1.3 per cent. of ash. This was mainly barium sulphate and silica, introduced unavoidably in previous operations; as no way was found of removing this inorganic material, the necessary correction was made in the following analyses, which proved that the product is not dihydroxyadipic acid.

0.1253 gave 0.2056  $\text{CO}_2$  and 0.0598  $\text{H}_2\text{O}$ .  $\text{C}=44.73$ ;  $\text{H}=5.33$ .

0.1758 „ 0.2902  $\text{CO}_2$  „ 0.0823  $\text{H}_2\text{O}$ .  $\text{C}=44.99$ ;  $\text{H}=5.23$ .

$\text{C}_6\text{H}_{10}\text{O}_6$  requires  $\text{C}=40.42$ ;  $\text{H}=5.66$  per cent.

$\text{C}_6\text{H}_8\text{O}_5$  „  $\text{C}=44.95$ ;  $\text{H}=5.03$  „

The *silver salt* was prepared in the usual way from a neutral solution of the ammonium salt; it was dried over sulphuric acid and analysed.

0.1871 silver salt gave, on ignition, 0.1078 Ag.  $\text{Ag}=57.63$ .

0.1692 „ „ „ 0.0976 Ag.  $\text{Ag}=57.68$ .

$\text{C}_6\text{H}_8\text{O}_5\text{Ag}_2$  requires  $\text{Ag}=55.09$  per cent.

$\text{C}_6\text{H}_6\text{O}_5\text{Ag}_2$  „  $\text{Ag}=57.73$  „

These analyses, showing the silver salt to be dibasic but with the composition  $\text{C}_6\text{H}_6\text{O}_5\text{Ag}_2$ , make it very improbable that the acid  $\text{C}_6\text{H}_8\text{O}_5$  is the  $\delta$ -lactone of dihydroxyadipic acid; it must, in fact, be regarded as a tetrahydrofurfurandicarboxylic acid. This conclusion is supported by the fact that the same silver salt was obtained, without the previous isolation of the acid  $\text{C}_6\text{H}_8\text{O}_5$ , directly from an aqueous solution of dihydroxybutanetetracarboxylic acid, heated at  $170^\circ$  in a sealed tube for 6 hours, and then evaporated on a water-bath with addition of water to ensure the removal of carbon dioxide.

0.1779 gave 0.1214  $\text{CO}_2$ , 0.0286  $\text{H}_2\text{O}$ , and 0.1019 Ag.  $\text{C}=18.60$ ;  $\text{H}=1.80$ ;  $\text{Ag}=57.28$ .

$\text{C}_6\text{H}_6\text{O}_5\text{Ag}_2$  requires  $\text{C}=19.24$ ;  $\text{H}=1.62$ ;  $\text{Ag}=57.73$  per cent.

As stated in the introduction, the acid  $\text{C}_6\text{H}_8\text{O}_5$  began to melt at about  $65^\circ$ , but on raising the temperature the fusion proceeded only gradually and was not complete until about  $120^\circ$ . This absence of a definite melting point could not be attributed to impurity, or to the material being a mixture of entirely different substances in view of the analytical results adduced above, and pointed rather to the

possibility of the substance consisting of a mixture of stereoisomeric acids.

After preliminary experiments had shown that fractional crystallisation from water, although tedious, promised to effect a separation, the method was carefully applied to 32 grams of the tetrahydrofurfurandicarboxylic acid.

*Tetrahydrofurfuran-2:5-dicarboxylic Acid, m. p. 123—125°.*

Thirty-two grams of the acid  $C_6H_8O_5$  were dissolved in water, and the aqueous solution evaporated slowly to a small bulk on the water-bath, filtered from a little sediment of barium sulphate, and placed over sulphuric acid in a vacuum, when star-shaped clusters of crystals soon began to appear. As soon as at least half of the product had crystallised, the crystals were separated as completely as possible from the brown, syrup-like mother liquor by the aid of a pump and dried over sulphuric acid. They melted between  $90^\circ$  and  $122^\circ$ . On repeating the fractional crystallisation, 6 grams of beautiful, white crystals were ultimately obtained which melted at  $123—125^\circ$ ; after solidification, they melted again at the same temperature. The crystals had the same melting point, whether dried at  $100^\circ$  in a steam oven or by exposure in the air.

On analysis, the substance proved to have a composition corresponding to that of tetrahydrofurfurandicarboxylic acid.

0.1372 gave 0.2264  $CO_2$  and 0.0628  $H_2O$ . C = 44.98; H = 5.12.

$C_6H_8O_5$  requires C = 44.95; H = 5.03 per cent.

The acid has a very acrid taste. It is extremely soluble in cold water, methyl or ethyl alcohol, acetone, or glacial acetic acid, but is not readily dissolved by ether, and is practically insoluble in chloroform, benzene, or light petroleum. It dissolves in boiling toluene, and is rapidly precipitated, on cooling, in arborescent masses of minute crystals. It can be crystallised from a concentrated aqueous solution and from a very strong solution of hydrochloric acid. The acid is charred extremely readily if cautiously heated in a dry test-tube.

A neutral solution of the ammonium salt does not readily yield a precipitate on the addition of solutions of metallic salts, except in the case of silver and mercurous salts.

The *silver salt* of the acid was prepared and analysed both by ignition and by combustion. It was found impossible to estimate the carbon accurately, on account of the great tendency of the salt to explode, even at a very moderate temperature.

0.2984 gave 0.1704 Ag. Ag = 57.10.

0.2248 „ 0.1374 CO<sub>2</sub>, 0.0382 H<sub>2</sub>O, and 0.1291 Ag. C = 16.66;  
H = 1.90; Ag = 57.40.

C<sub>6</sub>H<sub>6</sub>O<sub>5</sub>Ag<sub>2</sub> requires C = 19.24; H = 1.62; Ag = 57.73 per cent.

The *basicity* of the acid was determined by titration with a solution of pure barium hydroxide, of which 1 c.c. contained 0.007607 gram Ba(OH)<sub>2</sub>.

0.4160 gram acid required 58.9 c.c. or 0.4480 gram Ba(OH)<sub>2</sub> for neutralisation, whether phenolphthalein or litmus was used as an indicator.

Calculated for C<sub>6</sub>H<sub>6</sub>O<sub>5</sub>, 0.4452 gram, and for C<sub>6</sub>H<sub>10</sub>O<sub>6</sub>, 0.4002 gram of Ba(OH)<sub>2</sub> would be required to form a dibasic salt with this amount of acid, a difference equivalent to 6 c.c. of solution.

An attempt was made to open the ring by boiling half a gram of the acid, dissolved in a little water for 6 hours, in a small Geissler flask. The silver salt was then prepared and analysed, proving that no change had occurred; a result which made it still less probable that the substance could be a  $\delta$ -lactone.

0.2292 gave 0.1316 Ag. Ag = 57.41.

C<sub>6</sub>H<sub>6</sub>O<sub>5</sub>Ag<sub>2</sub> requires Ag = 57.73 per cent.

C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>Ag<sub>2</sub> „ Ag = 55.09 „

*Tetrahydrofurfuran-2:5-dicarboxylic Acid, m. p. 93—95°,  
and its Hydrate.*

The brown, syrup-like mother liquor obtained in the course of the isolation of the acid of higher melting point was placed over sulphuric acid in a vacuum, but, even after standing some days, crystallisation did not begin until a fragment of the acid melting at 123—125° was added, and the solution vigorously stirred with a glass rod, when a pasty, crystalline mass resulted. This was at once filtered by means of a pump, and gave about 5 c.c. of a reddish-brown mother liquor and 11 grams of small, nearly white, sand-like crystals, which, after being spread on a porous plate, were found to melt gradually between 50° and 65°. The crystals were dissolved in a little cold water, and the solution, after filtration from a slight sediment, allowed to evaporate slowly over sulphuric acid in a vacuum until it became syrupy, without, however, any separation of crystals occurring, but on adding a small fragment and stirring the syrup suddenly became almost solid with sensible evolution of heat. The product was dried in the air on a porous tile, giving 8 grams of small, white crystals, which were found to melt at 56.5—62° and when dried over solid caustic potash in a vacuum,

showed no change in the melting point. A small portion was more completely dried in a steam oven at  $100^{\circ}$ ; after melting, it did not solidify on cooling until scratched with a glass rod, when it at once became solid and brittle; it then melted at  $59-62^{\circ}$ .

A portion was also placed in a vacuum over sulphuric acid, and the next day was found to be caked together, crisp, and nodular; it then began to melt at  $63^{\circ}$ , but was not completely fused even at  $70^{\circ}$ . This raising of the melting point was subsequently found to be due to the partial dehydration of the hydrate of tetrahydrofurfuran-dicarboxylic acid (m. p.  $59-62^{\circ}$ ), the anhydrous acid having a higher melting point (see p. 115).

In the account of the isolation of these substances, mention is made of 5 c.c. of a reddish-brown mother liquor which might conceivably contain a compound of still lower melting point, although contaminated by impurities accumulated in the numerous processes of the preparation. Careful examination, however, failed to reveal the presence of any other substance.

*Hydrate of Tetrahydrofurfuran-2:5-dicarboxylic Acid*,  $C_6H_8O_5 + H_2O$ .—The small, white crystals (8 grams), which when dried in the air melted at  $56.5-62^{\circ}$ , proved to be a hydrate of tetrahydrofurfuran-dicarboxylic acid. Prior to analysis, the crystals were dried over solid caustic potash in a vacuum for 3 days; they gave a slight amount of ash after ignition (0.3 per cent.), and the necessary correction was applied to the analytical results:

0.1593 gave 0.2360  $CO_2$  and 0.0812  $H_2O$ . C=40.37; H=5.70.

0.1188 „ 0.1777  $CO_2$  „ 0.0633  $H_2O$ . C=40.76; H=5.95.

$C_6H_{10}O_6$  requires C=40.42; H=5.66 per cent.

$C_6H_8O_5$  „ C=44.95; H=5.03 „

This conclusion was confirmed by determining the *basicity* of the acid with a solution of barium hydroxide containing 0.007607 gram  $Ba(OH)_2$  per c.c.

0.4340 gram acid required 55.2 c.c., or 0.4201 gram  $Ba(OH)_2$  for neutralisation whether phenolphthalein or litmus was used as an indicator.

Calculated for  $C_6H_{10}O_6$ , 0.4176 gram, and for  $C_6H_8O_5$ , 0.4645 gram of  $(BaOH)_2$  would be required to form a dibasic salt with this amount of acid.

The formula  $C_6H_{10}O_6$  represents both dihydroxyadipic acid and also monohydrated tetrahydrofurfurandicarboxylic acid. The formation and analysis of the silver salt showed, however, that the substance was the latter.

The *silver salt* was prepared and dried at  $100^{\circ}$ :

0.1735 gave 0.1228  $\text{CO}_2$ , 0.0292  $\text{H}_2\text{O}$ , and 0.0991 Ag.  $\text{C} = 19.30$ ;  
 $\text{H} = 1.87$ ;  $\text{Ag} = 57.14$ .

$\text{C}_6\text{H}_6\text{O}_5\text{Ag}_2$  requires  $\text{C} = 19.24$ ;  $\text{H} = 1.62$ ;  $\text{Ag} = 57.73$  per cent.

From another preparation, made 3 years previously, a silver salt was prepared which gave  $\text{Ag} = 57.53$  per cent.

The hydrate of tetrahydrofurfurandicarboxylic acid is extremely soluble in cold water, methyl or ethyl alcohol, acetone, or glacial acetic acid, but is not at all readily soluble in boiling ether, and dissolves only sparingly in boiling benzene, toluene, or light petroleum. It is soluble in concentrated hydrochloric acid, but if the solution is stirred and left over solid caustic potash the hydrate can be induced to crystallise in beautiful, white plates.

Concentrated hydrochloric acid is therefore the only solvent from which the hydrate can be crystallised without very great loss. The crystallisation was carried out as follows: 3 grams of the hydrate were dissolved in a little water, the solution filtered from a very small amount of sediment, and hydrogen chloride passed into it until the solution was saturated. After concentration in a vacuum, a white, crystalline precipitate was induced to form by adding a crystal and stirring vigorously. The product was collected, washed with a little strong hydrochloric acid, spread on a porous tile, and dried over solid caustic potash in a vacuum. In this way, 1.3 grams were obtained, which on analysis proved to be the substance  $\text{C}_6\text{H}_{10}\text{O}_6$  unchanged in composition. It melted at  $63-64^\circ$ , and this may probably be taken as the correct melting point rather than  $56.5-62^\circ$ , the melting point before crystallisation from hydrochloric acid.

An aqueous solution of the hydrate is intensely acid. A neutral solution of its ammonium salt gives a white precipitate with silver or mercurous nitrate, but no precipitate with barium nitrate, calcium chloride, lead acetate, or mercuric chloride.

*Tetrahydrofurfuran-2:5-dicarboxylic acid, m. p.*  $93-95^\circ$ .—It has already been stated that, after the hydrate of tetrahydrofurfurandicarboxylic acid had been placed for 1 day over sulphuric acid in a vacuum, the crystals were found to be caked together and could no longer be melted below  $70^\circ$ . A portion of the hydrate, which had been recrystallised from hydrochloric acid and melted at  $63-64^\circ$ , was exposed for 8 days over strong sulphuric acid in a vacuum. It then melted at  $93-95^\circ$ . On analysis:

0.1513 gave 0.2486  $\text{CO}_2$  and 0.0700  $\text{H}_2\text{O}$ .  $\text{C} = 44.79$ ;  $\text{H} = 5.17$ .

$\text{C}_6\text{H}_6\text{O}_5$  requires  $\text{C} = 44.95$ ;  $\text{H} = 5.03$  per cent.

This result showed that the raising of the melting point was due to the loss of a molecular proportion of water, and was confirmed by

determining the actual loss in weight which occurred when the hydrate was exposed over sulphuric acid.

1.1737 gram of the hydrate lost 0.0638 gram or 5.4 per cent. in 1 day; at the end of 10 days, the weight remained constant, and 0.1235 gram had been lost, or 10.52 per cent. The calculated loss is 10.10 per cent.

A determination of the *basicity* of the substance (m. p. 93—95°) with a solution of barium hydroxide containing 0.00917 gram barium hydroxide per c.c. confirmed the conclusion that it had the composition  $C_6H_8O_5$ .

0.4342 gram required 50.39 c.c. or 0.4622 gram  $Ba(OH)_2$  for neutralisation, whether phenolphthalein or litmus was used as the indicator.

Calculated for  $C_6H_{10}O_6$ , 0.4176 gram, and for  $C_6H_8O_5$ , 0.4645 gram of  $Ba(OH)_2$  would be required to form a dibasic salt with this amount of acid.

The *silver salt* was prepared and analysed:

0.1752 gave 0.1227  $CO_2$ , 0.0295  $H_2O$ , and 0.1007 Ag. C = 19.08; H = 1.88; Ag = 57.46.

$C_6H_6O_5Ag_2$  requires C = 19.24; H = 1.62; Ag = 57.73 per cent.

It follows therefore that the substance  $C_6H_8O_5$  cannot be the  $\delta$ -lactone of dihydroxyadipic acid. When a portion of the tetrahydrofurfurandicarboxylic acid melting at 93—94° was dissolved in a little water and the solution allowed to evaporate over solid potassium hydroxide until dry, the product was found to melt at 57—62°. Further, on exposing some of the acid in the open air for 7 days, the melting point was lowered until it became 57—62°. There was not sufficient material for analysis. These results show that this tetrahydrofurfurandicarboxylic acid can be readily converted into its hydrate.

A portion of the expense incurred in this investigation was defrayed by a grant awarded by the Government Grant Committee of the Royal Society, for which the author desires to express his thanks.

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THE OWENS COLLEGE, MANCHESTER;  
AND ACKWORTH SCHOOL.

XII.—*The Atomic Weight of Nitrogen.*

By GEORGE DEAN, B.A.

CONSIDERING the large number of very definite and stable compounds in which nitrogen occurs as a constituent, it might have been expected that the atomic weight of nitrogen would be known with the greatest exactness. The readiness and accuracy with which nitrates may be converted into chlorides and *vice versa*, the determination of the percentage of silver in silver nitrate by synthetical and by analytical methods, the ratio between ammonium chloride or bromide and the silver required for complete precipitation, and many other exact processes seem fully to warrant this supposition, and to enable us to deduce directly the ratio of the atomic weight of nitrogen to those of both hydrogen and oxygen. A glance at the summary of results given below, however, will show that much work has still to be done before we know the atomic weight of nitrogen as accurately as we have every reason to believe it can be determined with the resources now at our command.

The experiments described in the following paper were undertaken with the view of deducing the constant from a combination of elements which had not hitherto been used for the purpose. Before entering upon the account of the method adopted here and the results obtained, it may be of interest to briefly consider the most important work done by previous investigators.

Both for variety of method and the number of experiments, the researches of Stas take the foremost place. Making oxygen the standard of comparison, and giving to it a value of 16, the different numbers obtained by him for nitrogen, with the respective methods employed, are as follows:

(1) Comparison of ammonium chloride and metallic silver	14.043
(2)       "       "       bromide       "       "	14.048
(3) Conversion of silver into silver nitrate. (Two series of experiments, the atomic weight having, in each series, two values, deduced respectively from the weight of silver nitrate before and after fusion).	
First series, silver nitrate before fusion.....	14.044
"       "       "       after       " .....	14.029
Second   "       "       before       " .....	14.054
"       "       "       after       " .....	14.042
(4) Comparison of ammonium chloride and silver nitrate..	14.027
(5) Conversion of potassium chloride into potassium nitrate	14.044
(6)       "       sodium       "       sodium       "	14.046

## (7) Comparison of silver nitrate and potassium chloride :

First series.....	14.083
Second „ .....	14.105
Third „ .....	14.043

The general mean of these values, assigning equal importance to each, is 14.051, the lowest value obtained being 14.027, the highest 14.105.

Next in order of importance to the work of Stas is probably that of Penny (*Phil. Trans.*, 1839, 129, I, 32); his various methods and the results respectively deduced from them may be briefly given thus :

(1) Conversion of metallic silver into nitrate .....	13.996
(2) „ „ silver nitrate into silver chloride.....	14.011
(3) „ „ potassium nitrate into potassium chloride	14.037
(4) „ „ „ chloride „ nitrate..	14.039
(5) „ „ „ chlorate „ „	14.003
(6) „ „ sodium „ sodium „	14.031
(7) „ „ „ chloride „ „	14.025
(8) „ „ „ nitrate „ chloride	14.021

The mean of these is 14.020, the lowest value being 13.996, the highest 14.039.

Marignac treated the question less exhaustively ; his methods with their corresponding results were :

(1) Comparison of metallic silver and ammonium chloride	13.961
(2) „ „ „ silver nitrate .....	13.977
(3) „ „ silver nitrate and potassium chloride...	14.150

the mean being 14.029.

Thus the values for the constant, determined by three of the masters in this branch of research, are practically 14.02, 14.03, and 14.05, the separate experiments yielding results varying from 13.961 to 14.150.

Other workers have used methods more or less similar with the following results.

Pelouze (*Compt. rend.*, 1845, 20, 1047) determined the weight of pure silver which, when dissolved in nitric acid, was sufficient for the complete precipitation of a weighed amount of pure ammonium chloride. The atomic weight of nitrogen calculated from his numbers is 13.975.

Hardin (*J. Amer. Chem. Soc.*, 1896, 18, 995) electrolysed small weighed amounts of silver nitrate, and weighed the silver deposited. His data lead to the value 14.042.

Turner (*Phil. Trans.*, 1833, 123, II, 537) converted a weighed



amount of silver nitrate into silver chloride, and determined the mass of chloride produced. His experiments give the value 14.013.

Hibbs (*J. Amer. Chem. Soc.*, 1896, 18, 1044) heated known masses of potassium nitrate in a stream of hydrogen chloride, and weighed the amount of chloride obtained. Moreover, the same process was applied to the sodium compound, the results being 14.032 and 14.026 respectively.

Thomsen (*Zeit. physikal. Chem.*, 1894, 13, 398) determined the ratio of the weights of hydrogen chloride and ammonia which combine with each other. He passed pure, dry hydrogen chloride into a weighed apparatus containing distilled water, and weighed again. Then pure ammonia was led in until it was present in slight excess, and the increase in weight observed, the excess of ammonia being finally determined by titration with standard acid. His mean result, 2.13934, leads to the value 14.021 for nitrogen.

Excluding the value deduced by Thomsen—to which little weight can be assigned as his experiments also lead to the conclusion that the ratio of H : O is 1:16 instead of 1:15.88 or 1:15.89 as established by the laborious researches of Rayleigh, Leduc, Morley, Scott, Noyes, and others—the mean is 14.034, if equal importance is given to the result of each separate series of experiments.

So far the results considered have been those which are based upon purely chemical methods. In the various determinations of the density of nitrogen, we have, on the other hand, a series of values obtained by physical means. The work of the earlier experimenters, Biot and Arago, Thomson, &c., was carried on without the refinements of accuracy brought to the aid of later research, and may be passed over here. More exact estimations have been made by Dumas and Boussingault, Regnault, von Jolly, Leduc, and Rayleigh, but chiefly with residual atmospheric nitrogen, and therefore still containing argon. In consequence of the admixture of this substance with the nitrogen, these results also are of little value for our present purpose. The most recent numbers obtained for *pure* nitrogen, both by Lord Rayleigh and M. Leduc, however, are almost identical. Taking oxygen as the unit, Leduc, from his own experiments, gives to nitrogen a density of 0.87508, and from Rayleigh's data, 0.87507 (*Compt. rend.*, 1898, 126, 415). Lord Rayleigh refers his results to the density of *air* as unit, and obtains for nitrogen and oxygen the densities 0.96737 and 1.10535 respectively; hence the relative densities are 14.003:16 (*Proc. Roy. Soc.*, 1897, 62, 209).

Now the great similarity in behaviour of oxygen and nitrogen, with regard to changes in temperature and pressure, renders it almost impossible that any deviations from Avogadro's law would be able to reconcile the two values of 14.034 as found by chemical methods and

14.003 by physical methods. This view is supported by D. Berthelot's recalculation of the atomic weight of nitrogen from the densities of nitrogen and oxygen, on the assumption that Avogadro's law is strictly accurate at low pressures. After applying a correction for the differences in compressibility of the two gases, the ratio is only raised to 14.007:16 (*Compt. rend.*, 1898, 126, 954). It was therefore thought to be of the greatest importance to redetermine this constant by some new method involving as few atomic weights as possible, and only those which are known with the highest degree of accuracy.

### *Method Employed.*

Some years ago, when discussing the probable cause of the differences between Stas' numbers deduced from the weights of fused and unfused silver nitrate respectively, Professor Dewar suggested the use of silver cyanide in order to obtain an independent value. By determining the amount of silver in a known weight of cyanide, the equivalent of cyanogen could be estimated; by subtracting from this the atomic weight of carbon, that of nitrogen is obtained.

Many preliminary experiments were made before the final method of treatment was decided upon. Of course, the simplest plan, which at once suggested itself, was to heat a weighed amount of cyanide, and weigh the silver left. Unfortunately, the formation of paracyanogen and a carbide of silver in the mass of metal, and the appreciable volatility of silver when heated for a fair length of time in the air, led to an utter lack of agreement among the results obtained. Attempts were made, on the other hand, with varying degrees of success, to dissolve weighed amounts of the cyanide in nitric acid alone, in nitric acid with some other oxidising agent (for example, potassium permanganate), and in nitric acid under pressure, and to estimate the weight of silver in solution. Ultimately this difficulty was overcome, and the method resolved itself into the following steps:

- I. Preparation of pure silver sulphate;
- II.       "       "       hydrocyanic acid;
- III.       "       "       silver cyanide, free from sulphuric acid;
- IV.       "       "       nitric acid, free from haloid acids;
- V. Drying of the cyanide until its weight remained constant;
- VI. Conversion of the weighed cyanide into some soluble silver salt;
- VII. Estimation of the amount of silver in solution.

These objects were obtained in the following manner. First, ordinary silver nitrate was dissolved in water and precipitated by means of

redistilled sulphuric acid. The fine crystals of silver sulphate were drained, recrystallised twice from a large volume of distilled water, and finally made up into a dilute solution. Next, a weak solution of hydrocyanic acid was prepared by the following method. Potassium ferrocyanide was recrystallised in a fine state of division, and distilled with dilute sulphuric acid, in an apparatus so arranged that any liquid thrown up in the act of ebullition was reflected back into the flask. The distillate was finally redistilled over a little magnesium carbonate, which was used to prevent "bumping" chiefly, but also to combine with any traces of sulphuric acid which might be present.

The silver sulphate solution was placed in a stoppered bottle, dilute hydrocyanic acid added, and the whole well shaken, to render the precipitate flocculent. More acid was added, and the process repeated until all the silver was precipitated as cyanide; the clear liquid was then poured off, and more sulphate solution added and precipitated in a similar manner. When a suitable quantity of cyanide had been obtained, it was repeatedly washed with cold, and finally with hot distilled water, and allowed to stand for some weeks, the water being occasionally renewed. Any traces of sulphate of silver enclosed in the flocculi would thus have the opportunity of diffusing out. The cyanide was finally dried, as described later.

*Nitric Acid.*—The "pure" acid of commerce, sp. gr. 1.42, was twice redistilled, the first time with a few drops of silver nitrate solution, precautions being taken to avoid spittings being carried over into the distillate. The acid finally collected, on being tested in the Stas chamber, was absolutely free from either hydrochloric acid or silver.

*Potassium Bromide*, used in determining the amount of silver in solution.—For this I am indebted to the kindness of Dr. Scott, Superintendent of the Davy-Faraday Research Laboratory. It is part of the sample used by Dewar and Scott in their determination of the atomic weight of manganese (*Proc. Roy. Soc.*, 1883, 35, 44), and was prepared from potassium carbonate, obtained by decomposing carefully recrystallised potassium bitartrate, and pure hydrobromic acid, obtained from the distillation of potassium bromide and sulphuric acid somewhat diluted.

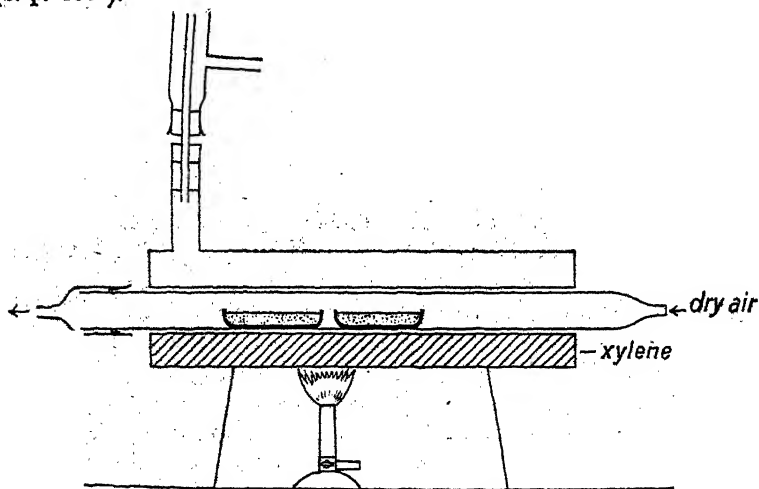
#### *Drying of the Silver Cyanide.*

The carefully washed precipitate was placed in a clean porcelain basin and as much as possible of the water poured away. After heating for about 12 hours in a steam oven, the basin was placed over concentrated sulphuric acid in a vacuum desiccator, which was then exhausted. The salt was left drying in this manner for a week, the surface of the acid being renewed by occasional agitation. A portion was then transferred to two platinum boats, which were enclosed in thin

glass tubes, sliding the one over the other, and fitting fairly tightly, to prevent moisture being absorbed from the air. The whole—case, boats, and cyanide—was then weighed. The actual numbers obtained throughout in one determination are given below.

July 11th, 1898. Boats + tubes + cyanide. 67.947 grams.

The boats were afterwards placed in a wide glass tube, drawn out at one end, and connected there with a series of U tubes, &c., containing calcium chloride, phosphoric oxide, solid caustic potash, &c. Over the other end fitted a slightly wider tube, also drawn out at one end, and connected through a drying tube with a water pump. By means of this arrangement, a slow, steady current of pure, dry air (freed from traces of carbon dioxide and sulphuretted hydrogen by passage through a series of potash bulbs) could be drawn over the cyanide. The tube containing the boats was kept at a fairly high temperature by means of an annular heater containing boiling xylene (b. p. 135°).



The boats were heated in this way in dry air, constantly renewed, for 17 hours, allowed to cool all night in the heater, transferred next day to the tubes, and weighed.

July 13th. Boats + tubes + cyanide. 67.9466 grams.

The cyanide had lost 1.1 milligrams in 17 hours. The boats were again placed in the tube and heated for 18 hours, allowed to cool as before, and weighed.

July 15th. Boats + tubes + cyanide. 67.94665 grams.

After 18 hours heating, the weight was thus practically unaltered.

*Solution of the Silver Cyanide.*

This was effected in a glass bulb of about 300 c.c. capacity, provided with a long neck. The end of the neck was turned out slightly, and had a small lip in order to make it easier to pour accurately. A small glass condenser was ground to fit into the neck of the bulb, the upper end of the condenser being again fitted with a set of three small bulbs, also ground in. By taking these precautions, all loss of liquid by spirting was effectually prevented.

The bulb was disconnected from the condenser, set up vertically over a sheet of paper, and a funnel placed in the neck. To transfer the cyanide, the boats were carefully lifted over the funnel and gently tapped, any granules remaining on the sides of the funnel being finally washed in by means of pure nitric acid. The boats and tubes were then weighed.

Boats + tubes .....	55.8347 grams.
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Weight of cyanide taken .....	12.11195 ,,
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In all 60 c.c. of nitric acid were added, the bulb then attached to the condenser, and the contents kept gently simmering on a sand-bath until the solid had completely dissolved. This took place in about 40 hours, thorough conversion into nitrate being marked by the "bumping" of the liquid.

It was found that *fuming* nitric acid did not dissolve the silver cyanide nearly as readily as the 68 per cent. acid, on account of the insoluble nitrate being precipitated upon it, and protecting it against further action.

*Determination of the Silver.*

For this, the bulbs and condenser were carefully rinsed into a large stoppered bottle by means of distilled water and the contents of the large bulb added. The latter was repeatedly washed by boiling a little water in it and allowing the condensed water to run down the sides, the different washings being added to the main portion of the liquid. Next the amount of potassium bromide necessary for the theoretical weight of silver present was calculated, and weighed out into a small beaker. In the particular experiment under consideration, the weights were those given below:

July 20th. Beaker .....	11.8087 grams.
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„ + bromide .....	22.5716 ,,
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Weight of potassium bromide taken...	10.7629 ,,
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In order to protect the silver bromide, when precipitated, from the action of the light, the bottle containing the silver solution was wrapped in red paper. The weighed amount of potassium bromide in the beaker was dissolved in a little distilled water, and the solution transferred with the utmost care to the silver solution. Finally, the bottle was vigorously shaken at intervals in order to procure a perfectly clear liquid above the precipitated silver bromide, and allowed to stand for a day.

The next step was the estimation of the amount of silver or potassium bromide present in excess. Standard solutions of these substances were employed (1 gram of the former containing 0.00117 gram of silver, and 1 gram of the latter being equivalent to 0.00094 gram of silver) and small quantities added from weighed stoppered burettes until the end point was determined, that is, until further addition produced no turbidity. The weight of solution added furnished the weight of silver or bromide needed, and this, with the weight of bromide originally added, gave the means of determining the exact weight of silver in the weight of silver cyanide taken.

The titration was performed in a dark room, a double box similar to that used by Stas being employed to hold the vessel and lamp. Yellow light was passed through the upper portion of the clear liquid in the bottle, and a few drops of the standard solution of silver or potassium bromide, as the case might be, were added to determine which was in excess. Then five or six drops of solution were run in at a time until it was known that a slight excess had again been added. This excess was carefully titrated by means of the other solution, added a drop or so at a time. In the experiment cited above, the weights of the solutions used before complete precipitation was ensured were:

July 23rd. Potassium bromide 1.175 grams = 0.00110 grams silver.  
 Silver ..... 0.30     "     = 0.00035     "

#### *Corrections.*

Having now obtained all the experimental data, the various corrections for buoyancy and for discrepancies between the actual masses of the weights used and their face values had to be applied. The former were obtained by means of the following densities: Silver cyanide, 3.94; potassium bromide, 2.69; brass, 8.4; air, 0.0012; silver, 10.6; the latter, by careful comparison of the set of weights among themselves and reduction to expression in terms of one of them. (The weight thus adopted as unit was the third gram weight, which is rarely used, and hence suffers little loss from abrasion, &c.) The

balance used was by Bunge of Hamburg, and the weights, a fine set of platinised brass weights, by Sartorius.

Silver cyanide as weighed at first .....	12.11195	grams.
Correction for buoyancy of cyanide + 0.00368		
"                    weights - 0.00175		
"                    weights ..... - 0.00171		
Total correction .....	+ 0.00022	„
Corrected weight of cyanide .....	12.11213	„
Potassium bromide as weighed at first.....	10.7629	grams.
Correction for buoyancy of bromide + 0.0048		
"                    weights - 0.00153		
"                    weights ..... - 0.00182		
Total correction .....	+ 0.00145	„
Corrected weight of bromide .....	10.76435	„

#### *Calculation of Equivalent of Cyanogen.*

Having obtained the exact weight of cyanide taken, the amount of silver contained in the cyanide is calculated from the weight of potassium bromide used; by simple proportion, the weight of silver cyanide which would contain the atomic weight of silver is estimated. This is its molecular weight. On subtracting the atomic weight of silver, the equivalent weight of cyanogen remains. The atomic weights used were those found by Stas, namely,  $\text{Ag} = 107.93$ ,  $\text{O} = 16$ . In addition, it was necessary to know the weight of the potassium bromide employed which would completely precipitate 100 parts by weight of silver; this was found to be 110.313 parts. The experiments conducted in order to ascertain this fact will be referred to later.

Weight of potassium bromide = 10.76435 grams.

Its equivalent of silver =  $\frac{100 \times 10.76435}{110.313} = 9.75800$  grams.

Equivalent in silver of the potassium bromide  
solution needed for complete precipitation ... = 0.00075 „

Total silver present ..... = 9.75875 „

Weight of silver cyanide = 12.11213 grams.

    "                    "                    containing 107.93 grams of silver =

$\frac{12.11213 \times 107.93}{9.75875} = 133.958$  grams.

Equivalent of cyanogen =  $133.958 - 107.93 = 26.028$ .

*Series of Experiments.*

In the following list are briefly given the leading data and the results of the different determinations. In experiment 6, the method of procedure was varied somewhat, the cyanide being converted in this case into *sulphate* instead of *nitrate* of silver. For this purpose, sulphuric acid, the "pure for analysis" of commerce, was redistilled in a vacuum, the first runnings being rejected. The cyanide was heated for some hours with the acid, diluted to nearly twice its volume with water, gas being gradually evolved and silver sulphate deposited. More of the concentrated acid was added and the heating repeated in order to bring the sulphate into solution, but although the crystalline salt seemed to disappear completely, there was a slight brownish, flocculent residue, possibly paracyanogen, still undissolved. The solution was ultimately transferred to a large volume of redistilled water, heated in a water-bath in order to have the sulphate in solution before adding the potassium bromide, and titrated in the usual way. The slight insoluble residue still remained on heating the diluted liquid.

The value deduced from this experiment is almost identical with that obtained in the one preceding it, which was performed by means of nitric acid.

Expt.	Wt. of AgCN.	Equiv. of Ag.	Mol. wt. of AgCN.	Equiv. of cyanogen.
1	6.2671 grams	5.0490 grams	133.969	26.039
2	17.60585 "	14.18496 "	133.956	26.026
3	17.1049 "	13.7801 "	133.979	26.049
4	17.9210 "	14.43881 "	133.960	26.080
5	12.11215 "	9.75875 "	133.958	26.028
6	14.6672 "	11.81727 "	133.959	26.029
	85.67820 grams	69.02889 grams	133.962	26.032

The mean value deduced from these experiments for the equivalent of cyanogen, calculating from the total weight of cyanide used and that of the silver found in it, is thus 26.032.

Before we can use this result in determining the atomic weight of nitrogen we must know that of carbon. F. W. Clarke, in his *Recalculation of the Atomic Weights*, gives, as the mean of all the important numbers determined by different experimenters, the value 12.011. Since then, however, Scott has shown that certain serious errors have hitherto been neglected, which render some of the experiments considered in that work useless for the time being. The best results



which are available, namely, those deduced from the combustion of a known amount of carbon and weight of the carbon dioxide formed, have been recalculated by him, and give a mean value of 12.001 practically (Trans., 1897, 71, 557). Subtracting this, then, from the cyanogen equivalent, we obtain for nitrogen an atomic weight of

14.031.

The accuracy of this number is, of course, strictly dependent upon the value for the atomic weight of carbon, and can only be relied upon to the same extent. The equivalent of cyanogen, however, is quite an independent value, cyanogen in the above experiments having been directly compared with silver, and, as far as method at least is concerned, its equivalent is of the same order of accuracy as those of chlorine, bromine, &c., and will be equally available for nitrogen or carbon as soon as the other constituent is evaluated.

*Remarks on the Titration.*

On titrating the excess of silver or bromide with the standard solution, the turbid cloud produced in the illuminated layer of liquid became less pronounced as this excess diminished. Moreover, after the excess had been totally precipitated and more of the solution added, a slight turbidity was produced on standing for a few minutes, which interfered with the accurate determination of the end point. With practice, however, it was possible to distinguish, to a drop or two, the point at which the excess had disappeared, as there was a difference in the appearance of the two turbidities. In order, however, to check the first determination, the addition of solution was continued in some cases until it was in excess, and the other solution added until the end point was again obtained. In one experiment, the numbers given for the equivalent by successive end point determinations made in this way were

(1) 26.0329.

(2) 26.0344.

The experience derived from many titrations has led to the same conclusion as that of Stas, namely, that titration of excess of silver by means of the bromide solution is more reliable than the converse process, and in most cases I have taken the result of the corresponding end point. From the numbers here quoted, however, an idea may be obtained of the magnitude of the maximum error likely to arise from this uncertainty.

In some of the earlier experiments, the titration was proceeded with on the same day as the potassium bromide was added. On repeating the addition of the standard solutions on the following day in order to

verify the end point, it was found necessary to add an extra amount of silver before precipitation was again complete. On following days, however, the liquid was quite free from either salt. It would appear that when the silver bromide is thrown down, the flocks enclose small quantities of potassium bromide which diffuse into the bulk of the liquid in the course of a day or so. In the later researches, provision was made for this, and the titration of the excess postponed for a day at least.

*Remarks on the Weighings.*

It was found that the weighings could be made quite easily to a tenth of a milligram, provided that the final weighing was not made until half an hour after the tubes and weights had been placed on the pans of the balance. Consecutive weighings, even after an interval of 12 hours, remained then absolutely constant. That the half-hour interval needed was not on account of a certain constant amount of hygroscopic moisture absorbed from the air by the material, is shown by the fact that the weighings taken immediately were always greater than those taken later.

*Estimation of the Silver Value of the Potassium Bromide used in the Titrations.*

In order to calculate the weight of silver present in solution from the weight of potassium bromide added, the amount of the latter equivalent to 100 parts of silver given by Stas, namely, 110.346, was at first made use of. As the results so obtained uniformly gave values for cyanogen which seemed abnormally high, I suspected that the bromide used in my research might contain small quantities of the sodium salt. A given weight of the bromide would thus be equivalent to a greater weight of silver than the pure salt, and the application of a corresponding correction would lead to lower molecular weight for silver cyanide and consequently a lower equivalent for cyanogen. The uncertainty arising from this cause was removed by obtaining directly the silver value of the bromide used. Varying quantities of carefully prepared silver were dissolved in nitric acid, purified in the manner described above, and titrated with the bromide in question in the usual way. In experiment A, the silver used had been obtained by the reduction of a solution of silver and copper nitrates by means of ammonium sulphite, Stas' directions concerning the method being scrupulously followed. Before the final weighing, the silver was heated in a covered porcelain crucible over a Bunsen burner.

In experiment B, a portion of the last fraction of silver prepared by the same method, but obtained on heating the solution, was taken,

heated to redness for some hours in a current of dry hydrogen (evolved by dropping water upon sodium), and allowed to cool, the gas still passing. This precaution was taken in order that all possible occluded oxygen might be removed from the silver.

In experiment C, the same sample of pure silver was used as in experiment B, but instead of being heated in hydrogen was simply heated in the flame of an alcohol burner in a covered crucible. The bromide used was heated in a current of dry air in a tube provided with a ground cap before being weighed, to insure its thorough freedom from moisture.

	Wt. of KBr taken.	Equivalent of Ag.	Wt. of KBr per 100 of Ag.
A.	9.40336 grams	8.52439 grams	110.311
B.	8.63900 „	7.83113 „	110.316
C.	9.84450 „	8.92422 „	110.312
Mean.....			110.313

The author has much pleasure in expressing his indebtedness to Professor Dewar for much kindly criticism and advice, and for the great interest he has taken throughout this investigation.

### XIII.—*Formation of $\alpha$ - and $\beta$ -Acrose from Glycollic Aldehyde.*

By HENRY JACKSON, B.A., Fellow of Downing College, Cambridge.

GLYCOLLIC aldehyde, first obtained in a dilute aqueous solution by Fischer and Landsteiner (*Ber.*, 1892, 25, 2549), was shown by these authors to lose its power of reducing Fehling's solution in the cold after treatment with 1 per cent. aqueous caustic soda at 0° for 15 hours. If the condensation product, after acidification with acetic acid, was heated with phenylhydrazine acetate on the water-bath for 8 hours, a crude osazone separated out which, after purification with ether and crystallisation, first from hot water and finally from dry benzene, gave a pure osazone which melted at 166—168° and had a composition very similar to that required for tetrosazone.

In 1897, Fenton found (*Trans.*, 71, 375) that when glycollic aldehyde in the form of a syrup is heated at 100° under very diminished pressure, it undergoes condensation, and by fractional solution with absolute alcohol he obtained a sparingly soluble portion which, on treatment with phenylhydrazine acetate, gave a normal hexosazone.

In a communication to the British Association this year, it was shown by Fenton and the author that if a dilute aqueous solution of glycollic aldehyde, prepared from dihydroxymaleic acid (Fenton, Trans., 1895, 67, 778) or glycol (Fenton and Jackson, Trans., 1899, 75, 2), is treated with dilute solutions of sodium or calcium hydroxides at the ordinary temperature of the laboratory (about 15°), it quickly undergoes condensation, losing its power of reducing Fehling's solution in the cold and of restoring the colour to an alcoholic solution of magenta, which had been decolorised by sulphur dioxide. After neutralising the product with acetic acid and warming on the water-bath for 3—4 hours with phenylhydrazine acetate, a beautiful, yellow osazone separated out on cooling, which, after crystallisation from boiling water, and afterwards from benzene and from ethyl acetate, melted sharply at 158°, and on analysis was found to be a normal hexosazone. Its melting point and action towards solvents pointed to its identity with  $\beta$ -acrosazone which Fischer and Tafel obtained from the condensation product of "glycerose" (Ber., 1887, 20, 3384).

Considering the readiness with which the condensation by alkalis took place at the ordinary temperature, it appeared to the author that it would be interesting to repeat the experiments conducted by Fischer and Landsteiner, and, with Mr. Fenton's approval, this has been done.

*Action of Dilute Caustic Soda Solution at 0° for 15 Hours.*

The details of the experiment were briefly as follows:—Pure glycollic aldehyde was diluted with distilled water until a solution containing 3 per cent. of the aldehyde was obtained, the strength being determined by Fehling's solution, as the reducing power of the pure aldehyde is known (Trans., 1899, 75, 579). To the solution, cooled to 0°, dilute caustic soda solution of known strength was added until the mixture contained 1 per cent. of the alkali. The combined solutions were then kept at 0° for 15 hours, when it was found that the liquid, which was originally colourless, had become orange-yellow. It still had the power of reducing Fehling's solution in the cold, although not so strongly as glycollic aldehyde, and also of restoring the colour to decolorised magenta solution.

After neutralising the condensation product with acetic acid, phenylhydrazine acetate was added in excess, and the mixture allowed to stand for 12 hours. The solution was then filtered and heated on the water-bath at 100° for 4 hours; longer heating was not found to materially increase the yield, whilst the osazone was far more resinous. After cooling and standing, a bulky, dirty yellow osazone separated out, which, after removal by filtration and drying in the air, was

rubbed with small quantities of dry benzene to remove the resinous matter, and then warmed with 50 times its weight of dry benzene. As only about half was soluble, the solution was quickly filtered on the pump from the sparingly soluble portion. The benzene solution, on standing, deposited a flocculent mass of yellow needles, which were collected and examined.

*Part soluble in Benzene.*—After being recrystallised from hot water and dried in the air, this fraction was crystallised twice from the least possible amount of boiling dry benzene. It was thus obtained as a mass of fine needles which melted sharply at  $167^{\circ}$ , and on analysis gave the following numbers, proving it to be tetrosazone :

0.1230 gave 0.2893  $\text{CO}_2$  and 0.0672  $\text{H}_2\text{O}$ .  $\text{C} = 64.15$  ;  $\text{H} = 6.07$ .

0.1452 „ 0.3409  $\text{CO}_2$  „ 0.0785  $\text{H}_2\text{O}$ .  $\text{C} = 64.03$  ;  $\text{H} = 6.01$ .

0.1710 „ 27.5 c.c. nitrogen at  $19^{\circ}$  and 758 mm.  $\text{N} = 18.50$ .

$\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4$  requires  $\text{C} = 64.43$  ;  $\text{H} = 6.04$  ;  $\text{N} = 18.9$  per cent.

These numbers agree closely with those obtained by Fischer and Landsteiner, and it would appear that tetrose is undoubtedly one of the condensation products of glycollic aldehyde.

*Part sparingly soluble in Benzene.*—This portion was again boiled with small quantities of dry benzene to remove all traces of tetrosazone. The osazone was dried in the air, and finally at  $100^{\circ}$  ; on analysis, it gave the following numbers :

0.1484 gave 0.3270  $\text{CO}_2$  and 0.0854  $\text{H}_2\text{O}$ .  $\text{C} = 60.23$  ;  $\text{H} = 6.37$ .

0.1660 „ 0.3655  $\text{CO}_2$  „ 0.0893  $\text{H}_2\text{O}$ .  $\text{C} = 59.91$  ;  $\text{H} = 5.98$ .

0.1120 „ 15.06 c.c. nitrogen at  $14^{\circ}$  and 749 mm.  $\text{N} = 15.80$ .

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$  requires  $\text{C} = 60.33$  ;  $\text{H} = 6.15$  ;  $\text{N} = 15.64$  per cent.

It was evident from these numbers that the substance was either a hexosazone or a mixture of hexosazones. It was therefore warmed with 10 times its weight of ethyl acetate, when only a portion dissolved ; the insoluble part was removed by filtration, and on standing a mass of yellow needles crystallised out from the solution ; this was recrystallised from hot water and finally from ethyl acetate. The osazone melted sharply at  $158^{\circ}$ . On analysis, the following numbers were obtained :

0.1380 gave 0.3042  $\text{CO}_2$  and 0.0746  $\text{H}_2\text{O}$ .  $\text{C} = 60.12$  ;  $\text{H} = 6.02$  per cent.

The osazone dissolves sparingly in ether or benzene, but easily in ethyl acetate, and is soluble in hot water. The analytical results, melting point, and action towards solvents point to its identity with  *$\beta$ -acrosazone*.

The portion sparingly soluble in ethyl acetate was left as a greenish-yellow powder. This was washed with small quantities of hot absolute

alcohol, and then crystallised from 95 per cent. alcohol. The osazone which separated out was next crystallised from 98 per cent. alcohol, and finally from hot absolute alcohol, in which it was sparingly soluble. It was thus obtained as a mass of yellowish needles, which were dried in the air and melted at 208—210°. On analysis, it was found to be a normal hexosazone :

0.1120 gave 0.2814  $\text{CO}_2$ . C = 60.42 per cent.

The melting point and sparing solubility towards solvents would point to the substance being  $\alpha$ -acrosazone, obtained by Fischer and Passmore from "formose" (*Ber.*, 1889, 22, 359), and by Fischer and Tafel from the condensation product of "glycerose" (*Ber.*, 1887, 20, 3384).

It would therefore seem that the condensation of glycollic aldehyde by dilute soda at 0°, if continued for a short time, results in the formation of tetrose and of  $\alpha$ - and  $\beta$ -acrose. The power which the product has of reducing Fehling's solution in the cold is probably due to tetrose, as it has been shown that the dilute aqueous solution of tetrose obtained by the oxidation of erythritol is able to effect the reduction in the cold (Fenton and Jackson, *Trans.*, 1899, 75, 1), whereas the two hexoses only bring this about on warming.

*Action of Dilute Caustic Soda Solution at 0° for 2 Days.*

In the next experiment, the condensation was allowed to go on for 2 days; the solution was then found to reduce Fehling's solution in the cold, but only to a very slight extent. It was neutralised with acetic acid, heated with phenylhydrazine acetate as before and the crude osazone rubbed with dry benzene. On heating with a large quantity of benzene, only a very small portion dissolved, the major portion being very sparingly soluble in this solvent. From the benzene solution, a small quantity of a bright yellow, crystalline osazone was obtained which, after drying, melted at 157°, and gave on analysis the following numbers, indicating that it was a mixture of tetrosazone with a hexosazone :

0.1635 gave 0.3725  $\text{CO}_2$  and 0.09  $\text{H}_2\text{O}$ . C = 62.12; H = 6.11 per cent.

By fractionation with dry ether, it was separated into two portions, tetrosazone being readily soluble whilst pure  $\beta$ -acrosazone is only very sparingly soluble in this solvent. The portion soluble in ether melted at 166°, and on analysis gave numbers corresponding to those required for tetrosazone :

0.0930 gave 0.2175  $\text{CO}_2$ . C = 63.86 per cent.

whilst the sparingly soluble portion melted at  $157^{\circ}$  and on analysis gave numbers corresponding to those required for a hexosazone.

0.1103 gave 0.2233  $\text{CO}_2$ . C = 60.7 per cent.

The major portion of the condensation product, namely, that sparingly soluble in benzene, was found on analysis to be a hexosazone, and was separated in the manner previously described into  $\beta$ -acrosazone melting at  $158^{\circ}$ , and  $\alpha$ -acrosazone melting at  $208^{\circ}$ .

*Action of Dilute Caustic Soda Solution at  $0^{\circ}$  for 6 Days.*

In the final experiments, the condensation was allowed to proceed until the solution did not reduce Fehling's solution after standing for half an hour in the cold. This was found to be case after the dilute aqueous solutions of glycollic aldehyde and caustic soda (1 per cent.) had remained at  $0^{\circ}$  for 6 days. The solution was neutralised with acetic acid and warmed with phenylhydrazine acetate as before. On boiling with benzene, only a small quantity dissolved, and this crystallised out as a mass of yellow needles which melted at  $158^{\circ}$ , and on analysis was found to consist of  $\beta$ -acrosazone mixed with a trace of tetrosazone.

0.1185 gave 0.2614  $\text{CO}_2$ . C = 60.60 per cent.

The major portion was, as before, separated into  $\alpha$ - and  $\beta$ -acrosazones. It would therefore seem that the tetrose formed by the condensation of glycollic aldehyde is unstable in the presence of dilute alkalis, and this view is emphasised by the fact that in the condensation at the ordinary temperature no tetrose could be found.

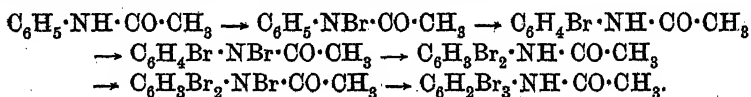
Glycollic aldehyde is the last member of the series of aldehydes from which synthetical hexoses can be obtained; the formation of  $\alpha$ - and  $\beta$ -acrose by its condensation is of much interest, as Fischer and his pupils have previously shown that the same sugars are formed by the condensation of formaldehyde and of glycerose.

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XIV.—*Substituted Nitrogen Chlorides and their Relation to the Substitution of Halogen in Anilides and Anilines. Part II. The Trichlorophenyl Acyl Nitrogen Chlorides.*

By F. D. CHATTAWAY and K. J. P. ORTON.

It has recently been shown by the authors (Trans., 1899, 75, 1046; Ber., 1899, 32, 3573)\* that substitution of chlorine and bromine in formanilide, acetanilide, and benzanilide is not a direct process, but that nitrogen chlorides and nitrogen bromides are first formed and subsequently undergo isomeric change. Thus, 2:4:6-tribromo-acetanilide, the ultimate product of the bromination of acetanilide, is the result of the following series of changes:



The tribromophenyl acyl nitrogen bromides are formed with great ease from the corresponding tribromoanilides, and we find that the same is the case with the nitrogen chlorides. The present paper contains an account of the latter compounds and of *p*-chlorophenyl benzoyl nitrogen chloride, which previously we were unable to obtain pure. These complete the series of nitrogen chlorides directly derivable from acetanilide.

The trichlorophenyl nitrogen chlorides show in most particulars the characteristic properties of the nitrogen halogen linking. They are well crystallised solids of low melting point, and dissolve readily in chloroform, but only sparingly in light petroleum, from which they can best be crystallised. They are, however, more stable than the corresponding mono- and di-chloro-derivatives, and the halogen can no longer be transferred to the ring, as this transference apparently occurs only when a para- or ortho-position relatively to the nitrogen is unoccupied. When these compounds are heated, isomeric change does not take place, but at a somewhat high temperature decomposition ensues and a tarry mass is formed.

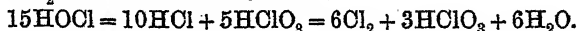
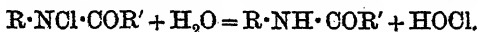
\* Since the publication of these papers, we find that we have overlooked a paper by Slosson (Ber., 1895, 28, 3265), in which he has repeated Bender's work and also prepared the nitrogen chlorides of form- and benz-anilide and the nitrogen bromides of form- and acet-anilide by a method similar in principle to ours. He has, however, only obtained one compound, phenyl formyl nitrogen chloride,  $\text{C}_6\text{H}_5\cdot\text{NCl}\cdot\text{CHO}$ , in a pure state. We extremely regret omitting to refer to this work in what we thought was a complete list of papers on the subject.



The ease with which the hydrogen attached to nitrogen is replaced by chlorine or bromine is in no way affected by the accumulation of halogen in the phenyl residue, and the conversion of 2:4:6-trichloroacetanilide, for example, into 2:4:6-trichlorophenyl acetyl nitrogen chloride takes place as readily as the corresponding replacement of the hydrogen attached to nitrogen in acetanilide itself.

As a further proof that formation of a nitrogen chloride or bromide in every case precedes substitution of halogen in the ring, it is interesting to note that the degree of ease with which the transformation of any substituted nitrogen bromide or chloride is effected corresponds with the ease or difficulty with which this transformation product is directly formed. As is well known, substitution by chlorine in anilides and anilines is never so easy as that by bromine\* and our experiments show that the bromides are always transformed with much greater readiness than the corresponding chlorides. For example, the transformation of 2:4-dichlorophenyl acetyl nitrogen chloride can only be effected by heating under pressure in a sealed tube, whilst that of 2:4-dibromophenyl acetyl nitrogen bromide takes place easily when the compound is heated on a water-bath.

On warming a substituted nitrogen chloride with any dilute acid on which hypochlorous acid has no action, a certain amount of hydrolysis always takes place, resulting in the regeneration of the anilide, liberation of chlorine, and formation of chloric acid.



This hydrolysis is much more marked with all the nitrogen bromides. It is also very noticeable in the case of the trichlorophenyl acyl nitrogen chlorides, but isomeric change takes place in most other nitrogen chlorides too readily to allow of this action proceeding to any large extent.

The fact that the halogen is directly attached to nitrogen in both the substituted nitrogen chlorides and bromides is shown by the exact correspondence of all the reactions which these compounds undergo with those which nitrogen iodide exhibits under similar conditions, as in the latter halogen can only be attached to nitrogen. The reactions of nitrogen iodide are, in fact, typical of the linking between nitrogen and halogens.

\* As an illustration we may point out that 2:4:6-trichloroacetanilide cannot be obtained under ordinary conditions by the direct chlorination of acetanilide, whilst 2:4:6-tribromoacetanilide is the chief product when an acetic acid solution of acetanilide is heated with an excess of bromine.

*2:4:6-Trichlorophenyl Formyl Nitrogen Chloride*,  $C_6H_2Cl_3 \cdot NCl \cdot CHO$ .

This compound is easily prepared by adding a slight excess of a solution of bleaching powder to 2:4:6-trichloroformanilide dissolved in warm acetic acid, and separates as an oil which quickly solidifies. It is readily soluble in chloroform or light petroleum (b. p. 80—100°), and crystallises from the latter in clusters of brilliant, white prisms with domed ends; it melts at 78°, and has all the characteristic properties of this group of compounds.

0.3227 liberated I = 24.92 c.c. *N*/10 iodine. Cl, as :NCl, = 13.68.

$C_7H_3ONCl_4$  requires Cl, as :NCl, = 13.69 per cent.

*2:4:6-Trichlorophenyl Acetyl Nitrogen Chloride*,  $C_6H_2Cl_3 \cdot NCl \cdot CO \cdot CH_3$ .

This compound is prepared from trichloroacetanilide exactly as the last-mentioned substance. It forms small, white, glistening, prismatic crystals resembling cubes in appearance, and melts at 74°.

0.1982 gave 0.4146 AgCl. Cl = 51.72.

$C_8H_3ONCl_4$  requires Cl = 51.94 per cent.

It is a comparatively stable substance, and when heated in a capillary tube does not show any sign of decomposition up to 190°. When heated, however, for many hours at 140° in a sealed tube, decomposition takes place, and acetyl chloride, 2:4:6-trichloroaniline, and 2:4:6-trichloroacetanilide can be recognised among the products.

*2:4:6-Trichlorophenyl Benzoyl Nitrogen Chloride*,  $C_6H_2Cl_3 \cdot NCl \cdot CO \cdot C_6H_5$ .

This substance is prepared from trichlorobenzanilide by the method described above. It crystallises singularly well in short, thick, lustrous prisms terminated by pyramids, and melts at 89°. As in the preceding cases, a nearly theoretical yield of this chloride is obtained.

0.3062 liberated I = 18.3 c.c. *N*/10 iodine. Cl, as :N·Cl, = 10.59.

$C_{13}H_7ONCl_4$  requires Cl, as :NCl, = 10.58 per cent.

When warmed with alcohol, this nitrogen chloride behaves like all the others (compare *loc. cit.*), and passes quantitatively back into 2:4:6-trichlorobenzanilide, ethyl hypochlorite which decomposes into aldehyde and hydrochloric acid being also formed.

*p-Chlorophenyl Benzoyl Nitrogen Chloride*,  $C_6H_4Cl \cdot NCl \cdot CO \cdot C_6H_5$ .

The preparation of this compound is rendered difficult by the sparing solubility of *p*-chlorobenzanilide, and at first (*loc. cit.*) we were

not able to obtain it except mixed with 2:4-dichlorophenyl nitrogen chloride.

It can, however, be prepared by using a hot alcoholic solution of the anilide, and allowing this to run slowly into a large excess of a solution of potassium hypochlorite containing potassium bicarbonate well cooled by a freezing mixture. Under these conditions, the nitrogen chloride suffers no transformation or decomposition, provided an excess of hypochlorous acid is always present, and the temperature not allowed to rise above  $0^{\circ}$  until the product is filtered off from the solution containing the alcohol.

*p*-Chlorophenyl benzoyl nitrogen chloride forms glistening, short prisms with domed ends, and melts at  $79.5^{\circ}$ .

0.3574 liberated  $I = 26.65$  c.c.  $N/10$  iodine.  $Cl$ , as  $\cdot NCl$ , = 13.24.

$C_{13}H_9ONCl_2$  requires  $Cl$ , as  $\cdot NCl$ , = 13.34 per cent.

On allowing a solution in glacial acetic acid to stand for some time well formed crystals of 2:4-dichlorobenzanilide slowly separate. This is often a very convenient method of effecting the transformation of nitrogen chlorides into the isomeric chloroanilides.

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## XV.—*The Decomposition of Chlorates, with Special Reference to the Evolution of Chlorine and Oxygen. Part I.*

By WILLIAM H. SODEAU, B.Sc.

THE ultimate object of this investigation is to ascertain the mechanism of the changes which take place when various chlorates are heated. These changes yield (in general) perchlorate, chloride, oxide, oxygen, and chlorine, but the relative proportions are known to vary very greatly with the nature of the base and with the mode of decomposition.

The present paper contains an account of experiments with barium chlorate and potassium chlorate, but other chlorates are being investigated, as also the mode of action of certain substances which facilitate decomposition. Throughout the paper, experiments are numbered in the order in which they were performed,

## EXPERIMENTAL.

I. *Evolution of Chlorine from Barium Chlorate.*

"Pure" barium chlorate of commerce was found to be neutral and free from strontium and calcium, but contained traces of dust and of chloride; after separating barium with sulphuric acid, the filtrate left only a trace of residue on evaporation. The salt was purified by careful recrystallisation, drained on a perforated porcelain plate (to avoid fibres of paper), and dried at  $135^{\circ}$  after powdering. Barium chlorate, unlike the potassium salt, has but little tendency to creep or spirt when decomposed; some care is necessary in order to ensure its regular decomposition, as a rise of temperature may render the action violent, the mass becoming red hot. The influence of variations of temperature upon the rate of decomposition of the salt at atmospheric pressure has been investigated by Potilitzin (*J. Russ. Chem. Soc.*, 1887, [1], 339; *Ber.*, 1887, 20, Ref. 769).

*Mode of Decomposition at various Pressures.*—A weighed quantity of the substance, usually 1 gram, was placed either in a soda-glass tube of 15 mm. bore closed at one end, or else in a platinum crucible contained in a closely fitting tube of about 28 mm. bore. The tube was then sealed on to a narrow one bent twice at right angles and ground into an absorption tube. When practicable, the gas was thus passed through pure potassium iodide solution (to which traces of iodine had been added until starch gave a faint coloration), and the liberated iodine was titrated with thiosulphate.\* In the later experiments at 1 mm. pressure, the chlorine was retained by potassium iodide dissolved in glycerol and distributed over glass beads. It will be shown that the amount of free chlorine must be found by examination of the residue.

Two decomposition tubes and a thermometer were usually clamped side by side in a bath of melted pewter, one tube being at atmospheric pressure and the other connected to a Geissler mercury pump having a bulb of 630 c.c. capacity, the upper neck of this being calibrated, in order that the pump might be used as a McLeod gauge; the mercury manometer was only relied on when the pressure amounted to several mm. The evolved oxygen was always roughly measured by displacement of water in order to observe the progress of the decomposition. Before raising the temperature to the decomposition point, the last traces of water were removed by heating the chlorate to about  $300^{\circ}$  for some time, the tube was then twice exhausted, dry air free from carbon dioxide being admitted. It was not found practicable to

\* The potassium iodide did not become alkaline; there was thus no evidence of the formation of ozone or of oxides of chlorine.

employ a constant temperature, for in order to avoid violent action at the commencement and yet complete the decomposition in the course of a few hours, it was necessary to gradually raise the temperature of the bath through  $70^{\circ}$  or more. The decompositions under reduced pressure took place, in general, at lower temperatures than those at atmospheric pressure, as equality in temperature would have necessitated a great difference in the duration of the experiment, owing to the marked manner in which reduction of pressure facilitates the decomposition, as shown in section III.

*Absorption of small amounts of Chlorine by Heated Glass.*—This was discovered by comparing the results of a few decompositions at 10–15 mm. with those at atmospheric pressure. Each decomposition lasted about two hours, and afterwards the residue and the contents of the absorption tube were titrated with hydrochloric acid and thiosulphate respectively. The original substance was perfectly neutral, and the standard solutions had been compared with each other by means of iodide and iodate of potassium.

Whether the substance was in a platinum crucible or placed directly in the tube, the amount of oxide in the residue, that is, its alkalinity, was but little influenced by the pressure, hence about the same amount of chlorine is evolved at 10–15 mm. and at atmospheric pressure. At 10–15 mm., the amount of chlorine reaching the potassium iodide was rather less than that lost by the residue, but at atmospheric pressure the contents of the absorption tube indicated no free chlorine, although sensitive to 1 drop  $N/1000$  iodine; on the other hand, the residue neutralised, for example, 6 c.c. of  $N/1000$  acid. It is thus evident that the chlorine had been absorbed by the heated glass. This absorption is lessened by reduction of pressure, or by passing a current of air, free from moisture and carbon dioxide, through the tube; treatment of the glass with steam is not an effective remedy.

*Examination of the Residues.*—Some experiments were conducted in order to ascertain the best method for titrating the oxide in the residue, this appearing to be the only reliable measure of the chlorine evolved. Phenolphthalein in the cold was found to be the most suitable indicator, as the large amount of barium chloride prevented the utilisation of the reaction between a slight excess of acid and a mixture of iodate (the iodine) and iodide of potassium to be titrated. As the total alkalinity is extremely small, it is important to avoid unnecessary dilution and to carefully guard against the presence of carbon dioxide. All the water used was boiled in a vacuum, and after this treatment 10 c.c. gave a pink coloration with phenolphthalein and 0.1 c.c. of  $N/1000$  baryta; the burettes were provided with guard tubes containing soda lime. Decinormal hydrochloric acid was diluted to  $N/500$  as required for use, the dilute baryta being titrated

against this in the cold and then boiled with excess in order to ascertain the slight correction for carbonate present. In an estimation, the residue was dissolved in a slight excess of  $N/500$  acid, boiled, quickly cooled in a desiccator containing soda-lime, and the excess of acid titrated with baryta; more acid was then added and the process repeated, in order to ensure the complete decomposition of any carbonate formed. This method was carefully tested and found to work well; owing to the dilution, there was no loss of acid on boiling nor were the titrations affected by addition of barium chloride or of neutralised barium peroxide.

To ascertain whether the presence of a trace of moisture during decomposition would introduce any considerable error, about 5 grams of finely powdered neutral barium chloride were introduced into a glass tube, a few drops of distilled water added, and the neck drawn out; this tube was placed in the bath during a slow decomposition (expt. 35) and the barium chloride heated in water vapour mixed with air for about 4 hours at  $360-400^\circ$  and then for 2 hours at  $400-480^\circ$ . The alkalinity corresponded to the loss of only 0.035 per cent. of the chlorine present, so that the precautions adopted to remove moisture appear to have been more thorough than was really necessary, the effect being small in comparison with the amount producing it.

Portions of several residues were examined for barium peroxide by adding 1 c.c. of  $N/1000$  permanganate to the solid, then a sufficiency of  $N/100$  hydrochloric acid, and some potassium iodide. On titrating the liquid with thiosulphate, the volume required was usually rather less than in blank experiments, but the difference was too small to afford satisfactory evidence of the presence of barium peroxide; the proportion in the final residue must therefore be exceedingly small; this may, perhaps, be accounted for by the high temperature at the end of the decomposition.

*Decomposition of the Chlorate* (see Table I).—Experiments made simultaneously in the same bath have been distinguished from each other by the letters *a*, *b*, and *c*. Those "in contact with platinum" took place in narrow platinum crucibles, each enclosed in a glass tube and covered with an overlapping split cone of platinum foil, the object of the cover being to prevent surface cooling and to retain any splashes; each crucible was used at atmospheric and reduced pressures alternately, in order to eliminate any possible difference between the pair. In 31*a*, some pieces of glass tube were placed in the crucible, but neither in this experiment nor in the decompositions in glass tubes was there any indication of action between the chlorate and glass.

It was necessary that the decompositions should last some hours when the pressure was to be kept at 1–2 mm. by means of the

mercury pump. At this pressure, the substance decomposed so much more readily that the temperature was at no stage raised to the fusing point of the mixture then present; at higher pressures, the mass always fused.

Where the duration is given as 0.5 minute, the decomposition was of a violent character, the mass becoming red hot. In expt. 47, the substance was dropped little by little into the already heated crucible (without the cone); the temperature would not rise so high as in the experiments just referred to, so this comes between the two other classes of experiments at atmospheric pressure. In the rapid decompositions, the amount of chlorine reaching the potassium iodide was comparable with that lost by the residue.

This series of experiments indicates that the proportion of free chlorine increases with the temperature, but is probably not affected by variations of pressure, as some allowance has to be made for the accompanying change of temperature (see theoretical part).

*Decomposition of a Mixture of Barium Chloride and Chlorate.*—H. Schulze (*J. pr. Chem.*, 1880, [ii], 21, 407) found that barium

TABLE I.—*Barium chlorate.*

No.	In contact with	Pressure.	Duration (minutes).	N/1000 HCl c.c. per gram.	Cl evolved (total = 100).	Mols. chloride Mols. oxide.
29c	Glass	1 atmosphere	0.5	48.8	0.74	134
31b	Platinum	"	0.5	41.8	0.63	158
46	"	"	0.5	49.2	0.75	132
47	"	"	*	32.3	0.50	199
33	Platinum	1—2 mm.	200	4.0	0.061	1640
34a	"	2 mm.	230	4.9	0.074	1340
35a	"	1 mm.	270	4.2	0.064	1560
29a	"	10—15 mm.	140	5.0	0.076	1310
32a	Glass	10—15 mm.	345	4.7	0.073	1400
29b	Platinum	1 atmosphere	140	5.5	0.082	1190
24b	"	"	250	6.1	0.093	1080
35b	"	"	340	7.4	0.112	890
45	"	"	50	5.0	0.076	1310
31a	Pt. and glass	"	90	7.3	0.111	902
44b	Glass	"	120	6.0	0.091	1090
44a	Glass and BaCl <sub>2</sub>	1 atmosphere	120	5.6	0.085	1170
42	Pt. and BaCl <sub>2</sub>	"	300	6.4	0.097	1030
43	"	"	180	4.7	0.073	1370

Rapid decomposition in small portions.

chloride remained perfectly neutral when heated to redness in dry oxygen, but supposed it to be partly converted into oxide by "nascent oxygen" when heated with potassium chlorate; the latter conclusion is traversed at the end of section III. The employment of *barium* chlorate avoids the possibility of double decomposition.

Some recrystallised barium chloride was roughly dried, finely powdered, and then dried at 155—160°, still remaining neutral. Mixtures having the composition  $\text{Ba}(\text{ClO}_3)_2 + 2\text{BaCl}_2$  were decomposed at atmospheric pressure in the same manner as the chlorate alone. It will be seen from Table I (p. 141) that the amounts of chlorine (or oxide) obtained from such mixtures agree with those obtained without added chloride, although the average amount of chloride present was then only one-fifth. It is thus evident that the added barium chloride was not attacked by the decomposing fused chlorate or by any of the products.

## II. *Decomposition Products of Potassium Chlorate.*

Several chemists have shown that pure potassium chlorate yields no free chlorine when decomposed in a platinum vessel under atmospheric pressure. On the other hand, Williams has stated (Proc., 1889, 5, 26) that the theoretical amount of oxygen was not obtained by heating the chlorate in a vacuum, that a gas, presumably chlorine, was given off which attacked mercury, and that the residue, therefore, probably contained peroxide.

The potassium chlorate used for the present work was obtained by repeated recrystallisation of the "pure" salt of commerce; special precautions were taken to avoid dust, &c., and the substance was finally dried at 115° after powdering. All the experiments with the substance in contact with glass were made before barium chlorate had been studied. Preliminary experiments indicated the absence of any considerable evolution of chlorine even when the pressure was reduced to a small fraction of a millimetre.

*Decomposition with Chlorate in contact with Glass.*—Portions weighing from 1 to 1.5 grams were decomposed in tubes of soda glass, Bohemian (combustion) glass, and Jena glass; the arrangement resembled that used for barium chlorate, but the tubes were heated either by radiation from an empty crucible or directly by means of a Bunsen burner provided with a chimney. The decompositions took place one at a time, and the results are given in Table II (p. 144).

In all these experiments, the amounts of free chlorine were very small. Before the decomposition of barium chlorate had been investigated, it was thought that the differences in experiments 19—22 indicated an evolution of chlorine under reduced pressure;



they are now regarded as showing that, at atmospheric pressure, the heated glass absorbs about 90 per cent. of the chlorine liberated by the action of the glass. The reabsorption of chlorine would (*ceteris paribus*) vary with the time of contact multiplied by the pressure (concentration) of the gas; this factor is given in the fifth column of Table II.

The amount of chlorine evolved seems to vary with the nature of the glass and with the mode of heating; the largest amount is obtained with Jena glass, its highly silicated nature probably causing a greater expulsion of chlorine and less reabsorption. It will be noticed that the heat of a flame seems to give rise to more action on the glass than the more evenly distributed radiation from a crucible; in either case, the greater part of the chlorine was evolved towards the end of the decomposition, when the temperature was sufficient to soften soda glass.

It has been repeatedly shown that potassium chlorate yields no free chlorine when decomposed at atmospheric pressure, yet in this series the largest amount was obtained in experiment 14; it is thus clear that the experiments of this series lead to fallacious results as regards the evolution of chlorine in the decomposition of the chlorate.

*Decomposition in Platinum.*—Except as indicated, the apparatus was identical with that used for barium chlorate. In the first pair of decompositions, the substance was decomposed in two narrow platinum crucibles each enclosed in a tube of Jena glass, one being kept at 10–15 mm. and the other at atmospheric pressure. The residues in the crucibles were neutral to phenolphthalein, but in each case some of the substance had reached the glass; this will account for the gas liberating a trace of iodine from the potassium iodide solution. On account of the tendency for potassium chlorate to creep and spirt, this series was not completed until after barium chlorate had been investigated and the best conditions ascertained.

In the final two pairs of decompositions, 40 and 41, each crucible contained 1 gram of potassium chlorate, and was covered with a piece of platinum foil bent round so as to form an inverted cone. The bath was kept at just over 400° for half an hour to drive off the last traces of moisture, and the tubes were then twice exhausted to 4 mm., dry air being admitted. The residues gave no pink colour with phenolphthalein even after boiling and cooling. A similar volume of water gave a very distinct pink with phenolphthalein and 0.1 c.c. of *N*/500 sodium carbonate, corresponding to 0.007 milligram of chlorine or 0.002 per 100 parts present. If, therefore, chlorine is evolved either at atmospheric pressure or at 1 mm., the amount cannot exceed this proportion. Determinations of free chlorine are evidently fallacious when the substance comes in contact with glass.

TABLE II.—*Potassium chlorate.*

No.	In contact with	Pressure.	Duration (minutes).	Duration × pressure.	Mode of heating.	N/1000 $\text{Na}_2\text{S}_2\text{O}_3$ c.c. per gram.	Cl obtained per 100 parts present.
13	Jena glass	10—15 mm.	120	1·9	Flame	1·4	0·017
14	"	1 atmosphere	35	35	"	6·0	0·074
23	"	"	50	50	Crucible	0·5	0·006
15	Soda glass	"	10	10	Flame	0·6	0·007
18	"	"	25	25	Crucible	0·12	0·0014
16	Bohemian	"	12	12	Flame	0·4	0·0047
22	"	"	100	100	Crucible	0·15	0·0018
19	"	10—15 mm.	100	1·6	"	1·6	0·019
20	"	"	150	2·4	"	1·2	0·015
21	"	"	150	2·4	"	1·3	0·016
40a	Platinum	1—2 mm.	240	0·5	} Melted pewter		Much less than 0·002 liberated
41a	"	1 mm.	330	0·4			
40b	"	1 atmosphere	240	240			
41b	"	"	330	330			

When either Bohemian combustion or soda glass was used, the first half of the gas contained only an infinitesimal amount of chlorine.

### III. *Experiments connected with the Rate of Decomposition.*

The mode of working was similar to that described on p. 138, potassium nitrate being occasionally substituted for metal in the bath on account of its transparency. The evolved oxygen was measured by displacement of water, or by collection over water in a graduated tube; in most experiments, the loss of weight was also determined.

*Potassium Chlorate under Reduced Pressure.*—Veley (*Phil. Trans.*, 1888, Pt. I. 282) has shown that the early stages of the decomposition are not influenced by reduction of the pressure to 20 mm., and the experiments described in section II appeared to indicate that variations of pressure had no influence upon the rate at any stage of the decomposition. This was more exactly proved by decomposing equal weights in a pair of similar bulbs, and, although one was at 1 mm. and the other at atmospheric pressure, the volumes of oxygen evolved from either agreed as well as could be expected during the whole of the six hours required for complete decomposition. This would seem to indicate that the formation of perchlorate is not greatly affected by variation of pressure, as otherwise a marked difference would be expected in the latter part of the decomposition.

*Barium Chlorate under Reduced Pressure.*—In this case, the previous experiments (section I) had indicated a very considerable facilitation in the evolution of oxygen, resulting from reduction of pressure. This has been confirmed by decomposing equal weights in paired bulbs. The temperature was kept fairly uniform during the first part of the decomposition, but was afterwards raised; readings were taken every five minutes. The general character of the results is indicated in the table.

Time.	O evolved (total=100).		Time.	O evolved (total=100).	
	At 1 atm.	10—15 mm.		At 1 atm.	1 mm.
45 mins.	6.2	22.2	80 mins.	1.6	24.7
60 "	13.6	41.5	140 "	4.7	37.7
75 "	22.9	55.7	200 "	10.1	41.9
90 "	31.7	59.2	260 "	20.2	45.6
160 "	49.1	60.5	320 "	39.9	49.1
315 "	67.5	85.5	400 "	43.7	52.6
			490 "	45.9	70.3

In the experiment recorded to the left, the temperature of the bath was about 380° (corr.) during the first 160 minutes; decomposition was practically complete (31.6 per cent. oxygen) after 400 minutes at atmospheric pressure, or 345 minutes at 10—15 mm. In neither experiment was there any *definite* break in the decomposition; further work will therefore be required in order to ascertain the influence of variation of pressure upon the proportion of perchlorate.

*Effect of Barium Chloride on the Decomposition of Barium Chlorate.*—The experiments described in the latter part of section I had shown that the presence of the chloride caused a marked retardation, as the temperatures of the bath had been higher than when barium chlorate was decomposed alone. The following table gives examples of the proportions of oxygen evolved during the decomposition of equal weights of barium chlorate alone and mixed with two molecular proportions of the chloride. Paired glass bulbs were used, and the total oxygen taken as 100.

Minutes.	30.	40.	50.	60.	65.	70.	85.	100.	110.	120.
Ba(ClO <sub>3</sub> ) <sub>2</sub> .....	9.0	25.4	38.6	45.9	50.7	51.6	56.6	73.8	95.9	100
Ba(ClO <sub>3</sub> ) <sub>2</sub> + 2BaCl <sub>2</sub> ...	4.9	6.6	10.7	13.2	26.2	50.0	52.5	70.5	96.7	100

The temperature of the bath was progressively raised; during the first part of the decomposition, the mixture did not reach a given

stage until the temperature was about  $20^{\circ}$  higher than when the pure chlorate attained the same degree of decomposition. It will be noticed that the chloride had very little effect after about half the oxygen had been evolved; a fair amount of chloride had then been formed by decomposition, and the temperature was much higher. Facilitation by reduced pressure and retardation by the addition of chloride may perhaps indicate an inverse action.

*Effect of Potassium Chloride on the Decomposition of Potassium Chlorate.*

—The two specimens of chloride used in these experiments were each prepared by decomposing some of the chlorate in a platinum crucible heated by a spirit flame. Equal weights of potassium chlorate, with and without addition of chloride, were decomposed in similar tubes; the volume of oxygen was noted at intervals of 1 to 2 minutes. A very slight *facilitation* was observed; taking the average of four pairs of decompositions, about one-third more oxygen was evolved in a given time when one molecular proportion of chloride had been added.

*Action of Heat on a Mixture of Potassium Chlorate and Barium Chloride.*—In this series of experiments, potassium chlorate and mixtures having the composition represented by  $2\text{KClO}_3 + \text{BaCl}_2$  and  $\text{Ba}(\text{ClO}_3)_2 + 2\text{BaCl}_2$  were heated in similar tubes, the quantities employed containing equal amounts of oxygen.

In comparing potassium chlorate with the mixture  $2\text{KClO}_3 + \text{BaCl}_2$ , the latter lost 59.1 per cent. of its oxygen in 35 minutes, but only 3.1 per cent. had been evolved from the pure chlorate; in another experiment, the mixture lost 10.7 per cent. of its oxygen with more gentle heating for 45 minutes, but the pure chlorate had then undergone no appreciable loss. Except in the early stages, the temperature required to produce a given rate of decomposition in this mixture is more or less comparable with that required for the mixture  $\text{Ba}(\text{ClO}_3)_2 + 2\text{BaCl}_2$ , and about  $50$ — $60^{\circ}$  lower than with potassium chlorate alone, although potassium chloride has but little effect and barium chloride markedly *retards* the decomposition of barium chlorate.

Fused barium chlorate has but little solvent action upon barium chloride, but potassium chlorate readily “dissolves” half an equivalent of it; hence, when the mixture  $\text{BaCl}_2 + 2\text{KClO}_3$  is heated, about half the barium chloride at once goes into solution. Under these circumstances, double decomposition must occur to a greater or less extent, and the ease with which the mixture is decomposed points to the continuous formation of barium chlorate, from which the oxygen is derived.

## THEORETICAL.

The proportion of chlorine liberated during the decomposition of chlorates by heat depends mainly on the nature of the base and the mode of heating. In order to explain this, two theories have been suggested. Schulze (*loc. cit.*) supposed the chlorate to decompose entirely into chloride and oxygen, the chlorine resulting from the action of "nascent oxygen" upon the chloride. W. Spring and Prost (*Bull. Soc. Chim.*, 1889, [iii], 1, 340), on the contrary, suggested that the chlorate decomposes entirely into oxide and chloric anhydride,  $\text{Cl}_2\text{O}_5$ , the latter immediately breaking up into chlorine and oxygen, more or less of the chlorine then reacting with the oxide to form chloride with the liberation of more oxygen.

It will be noticed that these explanations are in direct opposition, but in neither of the papers does there appear to be evidence that the suggested second action actually takes place under the conditions obtaining in the decomposition, nor does either deal with possible alternatives, of which there would seem to be two, namely, (1) the simultaneous formation of both oxide and chloride as *direct* products and (2) the simultaneous action of chlorine and oxygen upon the residue first produced.

For the purpose of discussion, it is convenient to classify the different reactions which might give rise to the formation of oxide and chloride (evolution of chlorine and oxygen) during a decomposition.

- (a) Chlorate giving chloride and oxygen.
- (b) Chlorate giving oxide, chlorine, and oxygen.
- (c) Chlorate acting upon chloride with liberation of chlorine.
- (d) Oxygen and chloride giving chlorine and oxide, apart from reverse action (e).
- (e) Chlorine and oxide giving oxygen and chloride, apart from reverse action (d).

(f) Simultaneous action of oxygen and chlorine, as in (d) and (e) combined.

*Decomposition of Barium Chlorate.*—Averaging three of the series of experiments given in Table I, we obtain the following:

Pressure.	Duration (minutes).	Duration $\times$ Pressure.	Total Cl=100		Mols. chloride Mols. oxide
			Free Cl.	Cl as chloride (by difference).	
1—2 mm.	233	0.5	0.066	99.934	1513
1 atmosphere	165	165	0.093	99.907	1077
"	0.5	0.5	0.704	99.296	141

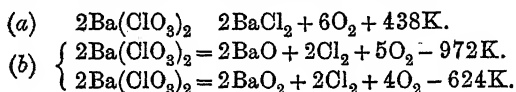
The action between a gas and a solid is usually increased by rise of temperature, and increases with the time of contact and the concentration of the gas; the two latter factors are included in the numbers given in the third column (duration multiplied by pressure in atmospheres). According to Spring and Prost, the chloride is produced by the action of chlorine upon the oxide first formed. Comparing the slow decompositions at 1—2 mm. and at 1 atm., we find that a slight fall of temperature combined with a reduction of the time-concentration factor from 165 to 0.5 has very slightly *increased* the amount of chloride from 99.907 to 99.934 per cent. of the possible amount, instead of very greatly decreasing it. Hence the chloride must be formed in another way, and Spring and Prost's theory does not hold for this chlorate.

Any reabsorption of chlorine which occurs is evidently not complete at atmospheric pressure, and would be much less so when the concentration of the gas is reduced by expansion (compare the experiments proving reabsorption by heated glass); such reabsorption therefore necessitates an increase of free chlorine on reduction of pressure, but none occurs at 1—2 mm., hence reaction (e) cannot occur to an appreciable extent. It may be noted that both oxide and chlorine are very greatly diluted with chloride and oxygen respectively. Comparing the effect of rapid decomposition at atmospheric pressure with that of reduction of pressure to 1—2 mm., we see that in either case the time-concentration factor has been reduced to about 0.5, yet this change has been accompanied by a slight *decrease* of chlorine in the latter case, but by a sevenfold *increase* in the former. The increase with rapid decomposition must therefore be due to the great rise of temperature instead of to rapidity of removal of the gaseous products as supposed by Spring and Prost. The increase does not really seem a necessary consequence of this theory, as the rapid formation of oxide would partly compensate for the decrease in the time, and the great rise of temperature might even cause more complete absorption by accelerating the reaction between oxide and chlorine. It seems probable that the proportion of free chlorine is not affected by variations of pressure and that the slight decrease at 1—2 mm. is due to reduction of temperature.

Schulze's hypothesis cannot apply to barium chlorate, for it has been shown that no chlorine is expelled from barium chloride by barium chlorate or any of its decomposition products under the conditions actually obtaining during a decomposition. It has also been noticed that the first bubbles of gas contained about the average proportion of chlorine, although only traces of chloride had then been formed. The chloride experiments exclude reactions (c) and (d), and show that, in this case, (f) coincides with (e), which has also been excluded; as chloride and oxide are actually formed, it is concluded

that reactions (a) and (b) occur during the decomposition, the average velocity of (a) being about 1000 to 1500 times that of (b) when the decomposition proceeds slowly, but at a higher temperature, when the decomposition is rapid, the ratio is only about 140:1. These average velocities represent the number of molecules of chloride to each molecule of oxide.

From the heats of formation, we obtain :



The result of rapid decomposition thus appears to be merely an example of an endothermic reaction (b) gaining upon an exothermic one (a) when the temperature is increased.

*Decomposition of Potassium Chlorate.*—In this case, the evidence is of a somewhat negative character, but as less than 0.007 milligram of chlorine is present in the 400 litres of gas (measured at about 530° and 1.5 mm.) from 1 gram of the substance, it seems extremely improbable that any appreciable amount is evolved at first. The last stages of the reabsorption would be exceedingly slow, as the oxide would then have been all but completely transformed into chloride; in the final residue, less than 0.002 per cent. of the potassium can remain as oxide. The improbability is increased by the fact that no such reabsorption was detected in the decomposition of barium chlorate at atmospheric pressure when the proportions of oxide and of free chlorine were respectively at least 50 times and 25,000 times those just given for potassium chlorate.

It appears that the direct decomposition into chloride and oxygen is the only one which need be considered, this proceeding at a rate at least 50,000 times as great as any reaction yielding chlorine.

#### *General Considerations.*

The experiments in this paper, and some already performed with lead chlorate and calcium chlorate but not yet published, tend to indicate the general conclusion that when a chlorate is heated it undergoes two simultaneous and independent decompositions, (a) into chloride and oxygen, (b) into oxide, chlorine, and oxygen; it remains to be shown that this view will harmonise with the results of Schulze's and of Spring and Prost's experiments. In each of these papers, a point is made of the increase of chlorine with increase of weakness of the base; now as the affinity for oxygen approaches that for chlorine, there would be more tendency for oxygen to attack the chloride, less for chlorine to react with the oxide, and more tendency for the oxide to be directly produced; this point therefore accords

equally with each of the three theories. The increase of chlorine with rapid decomposition has already been dealt with under barium chlorate; the only remaining point brought forward by Spring and Prost is the suggestion that the proportion of free chlorine is increased by addition of an acidic oxide because it combines with the liberated basic oxide and so prevents reabsorption of the chlorine first liberated. This cannot, however, be a generally correct explanation, for many such substances cause this action with potassium chlorate when 50—200° below the temperature at which this salt undergoes appreciable decomposition when heated alone (Baudrimont, *J. Pharm.*, 1871, [iv], 14, 81 and 161; Fowler and Grant, *Trans.*, 1890, 57, 272); the "liberated oxide" would then be non-existent. It does not seem remarkable that these substances should expel chlorine and oxygen (chloric anhydride) from chlorates, as many expel sulphuric anhydride from sulphates.

Schulze also shows that the amounts of free chlorine obtained by the decomposition of the chlorates of sodium, barium, and strontium agree with those resulting when equivalents of the chlorides are heated with potassium chlorate, and that comparable results would probably be obtained with other metals. Double decomposition, however, would be expected to take place with the formation of a chlorate more readily decomposed than that of potassium; these experiments would thus be decompositions of the respective chlorates rather than a study of the action of "nascent oxygen." In section III this has been shown to be the case with barium chloride, and there seems little doubt that the same will apply with other metals, as reaction takes place at a relatively low temperature.

It thus appears that the theory of two independent decompositions is in harmony, not only with the present investigation, but also with the results supposed to support the two older theories.

The author desires to express his thanks for facilities afforded him in the Davy-Faraday Research Laboratory.

## XVI.—*The Interaction of Sulphuric Acid and Potassium Ferrocyanide.*

By RICHARD HALIBURTON ADIE, M.A., B.Sc., and KENDALL COLIN BROWNING, B.A.

THE interaction of concentrated sulphuric acid and potassium ferrocyanide seems to have been first investigated by Döbereiner (*Schweiger's Journ.*, 1820, 28, 107), who stated that pure carbon monoxide is formed (compare Berzelius, *ibid.*, 1820, 30, 57).



Fownes (*Phil. Mag.*, 1844, [iii], 24, 21), apparently in ignorance of Döbereiner's previous work, to which he does not allude, found that nearly pure carbon monoxide is formed, accompanied at first with traces of hydrocyanic acid and carbon dioxide. The residue consisted chiefly of ferrous, ammonium, and potassium hydrogen sulphates. Towards the end of the reaction, ferric sulphate and sulphur dioxide were formed, and crystals of anhydrous iron ammonium alum deposited.

Merk (*Repert. Pharm.*, 1839, 68, 190), by rapidly distilling potassium ferrocyanide with sulphuric acid, obtained a distillate containing a little prussic acid, thiocyanic acid, and formic acid; he also obtained a sublimate of needle-shaped crystals of ammonium sulphite.

Everitt (*Phil. Mag.*, 1835, [iii], 6, 97) first showed that, with dilute sulphuric acid in slight excess, hydrocyanic acid is given off and a new salt, Everitt's salt  $K_2Fe_2(CN)_6$ , left.

Wittstein (*Vierteljahr. Pharm.*, 1854, 4, 515), Aschoff (*Arch. Pharm.*, 1860, [ii], 106, 257), and Williamson (*Annalen*, 1846, 57, 225, and *Memoirs Chem. Soc.*, 1848, 3, 125) also investigated the reaction.

Considering the differences between the conclusions of these investigators and the almost complete absence of quantitative results, the authors have investigated the decomposition of potassium ferrocyanide by sulphuric acid of concentrations varying from that of the approximately pure acid containing 98 per cent.  $H_2SO_4$ , to that of the acid represented by  $H_2SO_4 \cdot 18H_2O$ . The potassium ferrocyanide used was recrystallised until no impurity could be detected. It was dried at  $104-105^\circ$  until its weight was constant, and kept in a desiccator over phosphoric oxide. The sulphuric acid used was freshly distilled and was free from dissolved sulphur dioxide.

#### *Estimation of Carbon Monoxide.*

A weighed amount of ferrocyanide was introduced into a small flask or wide test-tube, which could be heated in an oil-bath, and the apparatus completely filled with dry carbon dioxide. The sulphuric acid was then run in by means of a tap-funnel and the vessel heated, a slow current of carbon dioxide being maintained. The carbon monoxide was collected over aqueous caustic potash (1:2). Temperatures were taken during the reaction by means of a thermometer immersed in the acid.

#### *Estimation of Hydrocyanic Acid.*

The anhydrous salt was placed in a flask and the apparatus filled with hydrogen, free from oxygen. The acid was run in and the mixture distilled into two sets of potash bulbs. In order to keep the concentration of the acid constant, a small double surface condenser was used, and at the end of each estimation its temperature was

raised to  $100^{\circ}$  to expel all traces of hydrocyanic acid \* from the apparatus. The solution was then washed out of the potash bulbs, diluted, and the hydrocyanic acid estimated by standard silver nitrate, using sodium chloride as indicator.

*Action of 98 per cent. Sulphuric Acid.*

When mixed with excess of 98 per cent. sulphuric acid, potassium ferrocyanide, dried as described, turned white and then dissolved. Although a trace of hydrocyanic acid was evolved at first, no carbon dioxide was given off and no measurable quantity of carbon monoxide was obtained, even after heating for two hours at  $100^{\circ}$ . When the temperature was raised to  $130^{\circ}$ , decomposition set in, but was slow even at  $200^{\circ}$ , at which temperature the acid fumed strongly, and sulphur dioxide was evolved.

Quantitative experiments showed that the reaction was very slow and incomplete. Carbon monoxide is only formed in any appreciable quantity at a temperature above  $200^{\circ}$ , and approximating to that of the formation of fumes. The action increased slowly on further raising the temperature, but even after  $2\frac{1}{2}$  hours at  $200-210^{\circ}$  the yield of carbon monoxide amounted only to about 4 per cent. of the theoretical, being dependent on the temperature and time of heating.

The authors confirm Fownes' observation of the formation of crystals containing potassium and ammonium ferric sulphates towards the end of the reaction.

To ascertain the nature of the reaction taking place in the solution, dry potassium ferrocyanide was dissolved in 48 per cent. sulphuric acid at  $100^{\circ}$  in an atmosphere of carbon dioxide, the solution cooled in a freezing mixture, and ether added. The white precipitate obtained was collected by the aid of a Pasteur filter in an atmosphere of hydrogen, dried, dissolved in absolute alcohol, and reprecipitated by ether. This process was repeated three times, and the white, crystalline product dried in a vacuum over phosphoric oxide. Its properties and determinations of the iron by means of mercuric oxide, and by sulphuric acid showed it to be hydroferrocyanic acid.

*Action of  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ .*

The reaction was carried out on similar lines to the foregoing, and, although more rapid, was still slow; gas bubbles appeared at about  $170^{\circ}$ , simultaneously with slight fuming. The action became more rapid at  $195-200^{\circ}$ , but was not complete at the end of an hour, even with a large excess of the acid. Thus 0.2832 gram of anhydrous

\* Blank experiments showed that hydrocyanic acid was completely expelled from the condenser by this means.

potassium ferrocyanide gave 85.8 c.c. (corr.) of carbon monoxide in 1 hour, the calculated volume being 103.4 c.c.

*Action of  $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ .*

The reaction was steady, the salt dissolved completely, and carbon monoxide began to be slowly evolved at about  $130^\circ$ . At  $175$ — $180^\circ$ , the evolution was rapid, and the reaction was complete in about 35—40 minutes. The yield of carbon monoxide accounted quantitatively for the amount of carbon in the ferrocyanide, and no measurable quantity of hydrocyanic acid could be detected.

		CO at $0^\circ$ and 760 mm.	
		Found.	Calc.
0.1388 gram $\text{K}_4\text{Fe}(\text{CN})_6, 3\text{H}_2\text{O}$ gave.....		44.6 c.c.	44.2 c.c.
0.2125    " $\text{K}_4\text{Fe}(\text{CN})_6, 3\text{H}_2\text{O}$ "    .....		77.6    "	78.0    "

*Action of  $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ .*

With increased dilution, the reaction began to change, hydrocyanic acid being formed in quantity, as well as carbon monoxide, and a small quantity of a solid substance was precipitated. A small quantity of formic acid was also detected, both in the absorption bulbs and in the flask. The carbon monoxide was given off below  $120^\circ$ , but the hydrocyanic acid only came off slowly, even with brisk boiling, at this temperature, as shown by the following three experiments:

Time.	HCN [calc. as 6HCN per mol. $\text{K}_4\text{Fe}(\text{CN})_6$ ].
$1\frac{1}{2}$ hours .....	2.6 per cent.
$3\frac{1}{2}$ "    .....	6.02    "
7       "    .....	8.80    "

Taking the highest of these numbers, we obtain

Mass $\text{K}_4\text{Fe}(\text{CN})_6$ .	Vol. CO at $0^\circ$ and 760 mm. (found).	HCN per cent. (found).	CN per cent. (calc.).
0.2241 gram.	6.99 c.c.	—	3.7
0.8964    "	—	8.83	8.43

The sum of these two amounts of cyanogen does not account for the whole of this radicle, the theoretical percentage being 36.96, so that the amount of formic acid obtained had to be estimated.

As it is difficult to estimate formic acid in presence of Everitt's salt, &c., by ordinary methods, it was determined from the amount of ammonia formed in the hydrolysis of the cyanide groups, as in the Kjeldahl method. The total ammonia obtained represents carbon monoxide as well as formic acid, hence the amount of the latter is obtained by subtracting the ammonia corresponding to the carbon monoxide from the total and calculating the difference as formic acid.

The amount of formic acid which was at a maximum with this

strength of acid\* was represented only in milligrams, and consequently was too small to affect the result.

The solid residue consisted of Everitt's salt, which is only slowly decomposed, mixed with a certain amount of ferrous and other sulphates in solution. Hence, in this case, the main products of the reaction are carbon monoxide and hydrocyanic acid, mixed in about the ratio 3.7 : 8.43.

*Action of  $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .*

With acids of less concentration than  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , for example  $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , the reaction showed a marked change in character,

Acid.	$\text{K}_4\text{Fe}(\text{CN})_6$ .	HCN [calc. as 6HCN per mol. $\text{K}_4\text{Fe}(\text{CN})_6$ ].	Time.
$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (Everitt's salt left)	0.7326 grams. 0.6997 " 0.8964 "	2.7 per cent. 6.3 " 8.8 "	1½ hours. 3¼ " 7 "
$\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Everitt's salt left)	0.9722 " 0.9432 " 0.8088 "	10.3 " 16.8 " 39 "	1½ " 3¼ " 6½ "
$\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ (Everitt's salt left)	2.2074 " 0.8463 " 1.1114 " 0.8536 "	24.5 " 36.6 " 47 " 71 "	2 " 2 " 3 " 6 "
$\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (No Everitt's salt left)	1.3180 " 1.1356 " 0.9382 "	30 " 98.7 " 99.2 "	1 " 3½ " 4½ "
$\text{H}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ (No Everitt's salt left)	1.0285 " 1.7694 " 1.0912 "	75 " 81 " 100 "	2½ " 5 " 6½ "
$\text{H}_2\text{SO}_4 \cdot 14\text{H}_2\text{O}$	0.8574 " 0.8642 " 0.7440 " 1.7230 " 1.0900 " 0.9796 "	47.2 " 57.0 " 65.0 " 80.5 " 86.0 " 94.8 "	1 " 2 " 3 " 3½ " 4 " 7½ "
$\text{H}_2\text{SO}_4 \cdot 16\text{H}_2\text{O}$	1.0848 " 2.0532 " 0.8896 " 1.5426 " 1.1634 " 0.9846 " 0.7461 " 0.9894 "	71.0 " 70.6 " 84.9 " 91.5 " 94.0 " 98.0 " 99.1 " 99.3 "	1 " 2 " 2 " 3 " 3 " 3 " 3¼ " 3½ "
$\text{H}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$	1.0766 " 1.1212 " 0.7394 "	98.7 " 98.2 " 99.0 "	2½ " 2 " 2 "

\* A number of experiments were made to see if formic acid could be prepared in quantity by modifying the action of  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  on potassium ferrocyanide, with, however, no satisfactory results.

hardly any carbon monoxide being obtained. Thus, 0.57 gram of potassium ferrocyanide heated for one hour with a large excess of  $\text{H}_2\text{SO}_4, 6\text{H}_2\text{O}$  in an atmosphere of carbon dioxide, gave less than 0.5 c.c. of carbon monoxide. The reaction began at about  $120^\circ$ .

The table on p. 154 contains a summary of the results obtained, using as nearly as possible the same weight of potassium ferrocyanide and a large excess of sulphuric acid, so as to keep the concentration of the acid nearly constant. The reaction in every case was carried out in an atmosphere of hydrogen as far as possible free from air. In all cases, traces of formic acid could be detected.

These results show that the theoretical yield of hydrocyanic acid was obtained by using acid of a concentration not exceeding that represented by  $\text{H}_2\text{SO}_4, 10\text{H}_2\text{O}$ .

At first, difficulty was experienced in obtaining consistent results. This was found to be due to

- (1) The rate at which the mixture was boiled.
- (2) The presence of traces of air.
- (3) The mass of potassium ferrocyanide used, the mass of acid being kept constant.

The effect due to the first cause is seen in the preceding table, by comparing, for example, the results obtained with  $\text{H}_2\text{SO}_4, 10\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4, 14\text{H}_2\text{O}$  respectively. The mixture was boiled much more rapidly in the case of the former.

The effect of the second cause is seen in the following table containing the results of experiments in which a very slow stream of air was used :

Acid.	$\text{K}_4\text{Fe}(\text{CN})_6$	HCN [calc. as 6HCN per mol. $\text{K}_4\text{Fe}(\text{CN})_6$ ].	Time.
$\text{H}_2\text{SO}_4, 6\text{H}_2\text{O}$	0.9432 grams.	54.5 per cent.	7 hours (air present)
	0.8088 "	39 "	6½ " ( " absent)
$\text{H}_2\text{SO}_4, 8\text{H}_2\text{O}$	0.9770 "	61.2 "	4½ " ( " present)
	1.1114 "	47 "	3 " ( " absent)
$\text{H}_2\text{SO}_4, 14\text{H}_2\text{O}$	1.9992 "	71.2 "	3 " ( " present)
	1.1031 "	75.2 "	3 " ( " " )
	0.7793 "	98.1 "	4 " ( " " )
	0.7440 "	65 "	3 " ( " absent)

The influence of the third cause, namely, that of mass, is seen in the following table, and becomes less with increasing dilution of the acid :

Acid.	$K_4Fe(CN)_6$ .	HCN [calc. as 6HCN per mol. $K_4Fe(CN)_6$ ].	Time.
$H_2SO_4, 8H_2O$	2.2074 grams. 0.8463 "	24.5 per cent. 36.6 "	2 hours. 2 "
$H_2SO_4, 12H_2O$	2.2826 " 2.1354 " 1.6285 "	60.2 " 66.6 " 75.5 "	3 " 3 $\frac{1}{2}$ " 2 $\frac{1}{2}$ "
$H_2SO_4, 16H_2O$	{ 2.0552 " 0.8896 " 1.5426 " 0.9846 "	70.6 " 84.9 " 91.5 " 98.3 "	2 " 2 " 3 " 3 "
$H_2SO_4, 18H_2O$	1.1212 " 0.7394 "	98.2 " 99.0 "	2 " 2 "

*Explanation of the Reaction.*

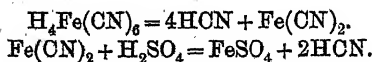
The reaction is probably explained in the following way. Hydroferrocyanic acid is first obtained, and can be isolated and examined. With strong sulphuric acid, it decomposes very slowly, evolving carbon monoxide, and forming ferrous and ferric sulphates, &c.

With an acid of the concentration  $H_2SO_4, 2H_2O$ , it decomposes quantitatively, forming carbon monoxide and ferrous, &c., sulphates. With sulphuric acid of less concentration, the following reactions occur.

(i) The hydroferrocyanic acid reacts with the potassium sulphate, forming Everitt's salt (Aschoff, *loc. cit.*):



(ii) At the same time, the hydroferrocyanic acid decomposes, forming  $FeSO_4$  and HCN.



This second reaction becomes more marked the greater the dilution, and predominates with an acid of the concentration  $H_2SO_4, 10H_2O$ , or with more dilute acids.

The second mode of decomposition explains the fact that with, for example,  $H_2SO_4, 18H_2O$ , the whole of the cyanogen is evolved as hydrocyanic acid rapidly and completely. If Everitt's salt were formed, the decomposition would take much longer, as this compound is only slowly decomposed by acid of this composition.

*Interaction of Hydroferrocyanic Acid and Potassium Sulphate.*

In order to investigate the reaction between hydroferrocyanic acid and potassium sulphate, aqueous solutions of varying strengths of

hydroferrocyanic acid were boiled with potassium sulphate solution in an atmosphere of hydrogen, a double surface condenser being used to keep the concentration constant. The water used had been boiled and also cooled in hydrogen to remove dissolved air.

In one case, a 10 per cent. solution of hydroferrocyanic acid with excess of potassium sulphate gave a precipitate of Everitt's salt on boiling. On warming the precipitate with dilute sulphuric acid at 60°\* and filtering, no ferrous sulphate was found in the filtrate, hence no ferrous cyanide was formed.

A 0.7 per cent. solution of hydroferrocyanic acid was similarly treated, and a precipitate obtained. It was, however, merely ferrous cyanide, as it rapidly and completely dissolved in dilute sulphuric acid at 60°, forming ferrous sulphate and evolving hydrocyanic acid.

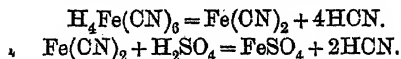
The precipitate obtained from the strong (10 per cent.) solution was collected in absence of air, washed repeatedly, placed in a desiccator in an atmosphere of carbon dioxide, and dried in a vacuum at 100° over phosphoric oxide. The pale bluish-yellow precipitate contained potassium, iron, and cyanogen, and was analysed by (i) evaporating down with strong sulphuric acid and a little ammonium sulphate and igniting; (ii) boiling with mercuric oxide, filtering, igniting, and weighing as ferric oxide.

0.3086 gave 0.1457  $\text{Fe}_2\text{O}_3$ .  $\text{Fe} = 33.1$ .

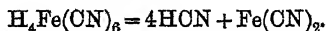
$\text{K}_2\text{Fe}_2(\text{CN})_6$  requires  $\text{Fe} = 32.4$  per cent.

#### *Decomposition of Hydroferrocyanic Acid.*

A number of experiments were made with the object of studying the decomposition represented by the equation:



According to Berzelius (*loc. cit.*) the decomposition with boiling water is represented by the equation:



Reemann and Carius (*Annalen*, 1860, 113, 39), and Étard and Bémont, (*Compt. rend.*, 1884, 99, 1024), on the other hand, express it by the equation:



but, in their papers, give neither analyses nor details.

To examine this question, a quantity of hydroferrocyanic acid was prepared by Possell's method, and purified by repeatedly dissolving in absolute alcohol and reprecipitating by ether until spectroscopically

\* Ferrous cyanide dissolves completely and rapidly at 60° in dilute sulphuric acid.

free from potassium. After drying in a vacuum over phosphoric oxide at 60°, this was analysed. Determination of the iron gave:

I.	II.	III.	Calc.
Fe 25.8	26.0	25.85	26.04 per cent.

On heating with water in an atmosphere of hydrogen, hydrocyanic acid began to be evolved at 60°, and a pale yellow-green solid separated out, thus proving Berzelius' statement to be correct. The hydrocyanic acid evolved was estimated as above.

0.4970  $\text{H}_4\text{Fe}(\text{CN})_6$  gave 0.2605 HCN. HCN = 52.4.

0.3863  $\text{H}_4\text{Fe}(\text{CN})_6$  „ 0.2035 HCN. HCN = 52.7.

3HCN requires 37.5 per cent. 4HCN requires 50 per cent.

The excess of hydrocyanic acid is undoubtedly due to hydrolysis of the ferrous cyanide, as on further boiling hydrocyanic acid is slowly evolved, and the precipitate, after drying in a vacuum, was found to contain ferrous oxide.

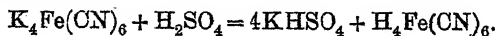
In presence of air, a coppery-blue precipitate was formed, but in too small a quantity for analysis. It was undoubtedly Williamson's blue,  $\text{KFe}_2(\text{CN})_6$ , as this is formed from Everitt's salt in presence of air and sulphuric acid (Williamson, *loc. cit.*). That Everitt's salt in presence of air is converted more or less completely to Williamson's blue, which, in the presence of dilute acid and oxygen, decomposes as fast as it is formed, was confirmed by preparing a quantity of the latter. On boiling this with dilute sulphuric acid in presence of air it dissolved, forming hydrocyanic acid and ferric sulphate.



#### Summary.

The preceding results may be epitomised:

(i) Concentrated sulphuric acid,  $\text{H}_2\text{SO}_4$ , dissolves potassium ferrocyanide and shares the potassium with the hydroferrocyanic acid. The ratio must be primarily determined by the active masses and relative affinities of the acids. The following equation represents the initial change:

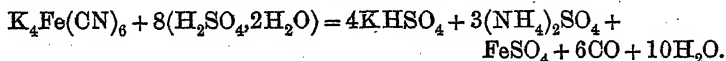


The solution is only very slowly decomposed by rise of temperature. Carbon monoxide is given off, but even at 200° the rate of evolution is low and the decomposition proceeds only when the sulphuric acid can dissociate or decompose into water, sulphur trioxide, and sulphur dioxide.

(ii) With the addition of water, marked decomposition occurs, and large quantities of carbon monoxide are formed. This reaction increases with dilution until the concentration  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  is reached;



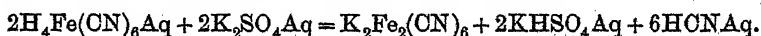
at this strength, the whole of the cyanogen appears as carbon monoxide at  $180^{\circ}$ . The equation which represents this change is:



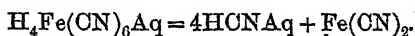
In this case, there is evidently hydrolysis, and it seems probable that it may be directly due to the molecules of water which are dissociated by solution in the solvent  $\text{H}_2\text{SO}_4$ . On the other hand, it is possible that sulphuric acid of the concentration  $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$  may really act as orthosulphuric acid,  $\text{S}(\text{OH})_6$ , in which case the above reaction may be evidence of its existence.

(iii) With further dilution to the concentration  $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$  there is another definite change in the reaction, since, in addition to carbon monoxide, Everitt's salt,  $\text{K}_2\text{Fe}_2(\text{CN})_6$ , and hydrocyanic acid make their appearance. That this is a definite change is shown by the fact that warm acid of the strength  $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$  immediately decomposes Everitt's salt.

The Everitt's salt appears to be formed from hydroferrocyanic acid by the action of potassium sulphate solution, thus:

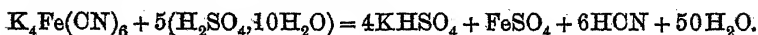


Some hydroferrocyanic acid is decomposed at the same time, forming hydrogen cyanide and ferrous cyanide. With increasing dilution, this becomes the more important and eventually, with acid of the concentration  $\text{H}_2\text{SO}_4, 10\text{H}_2\text{O}$ , the sole reaction. The equation which may represent this stage is:



In presence of the sulphuric acid, the ferrous cyanide dissolves with the formation of ferrous sulphate and hydrocyanic acid, and the change as a whole may be considered as due to the molecules of sulphuric acid dissociated by solution in the solvent water.

The final equation now becomes:



(iv) The final decomposition is hindered by increasing the mass of the salt, but helped by increase of temperature and the presence of air.

This last condition is important, and assists in the rapid decomposition of the salt. It also explains the use of porous brick or the passage of an air current to assist in the preparation of hydrocyanic acid on the manufacturing scale.

When air is present, Williamson's blue,  $\text{KFe}_2(\text{CN})_6$ , is formed in small quantity, and the solution contains ferric salts; it is probably formed from Everitt's salt, and then decomposed by the action of the oxygen of the air, as explained above.

These results, therefore, confirm the oldest account of the hydrolysis of hydroferrocyanic acid, namely, that due to Berzelius (*loc. cit.*).

The authors are engaged in further investigations of changes of the character of that described under (ii) produced by sulphuric acid, to see if they admit of further elucidation.

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## XVII.—*Action of Alkyl Iodides on the Mercuric Iodide Sulphides of the Fatty Series.*

By SAMUEL SMILES, B.Sc.

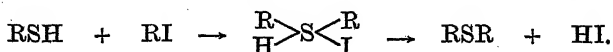
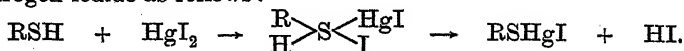
SOME years ago, Krüger (*J. pr. Chem.*, 1876, [ii], 14, 207) investigated the action of methyl iodide on methyl ethyl sulphide, and of ethyl iodide on dimethyl sulphide, and found that in each case a different dimethylethylsulphine iodide was produced. This work was repeated by Nasini and Scala (*Gazzetta*, 1888, 18, 67) a few years later and confirmed. Klinger and Maassen (*Annalen*, 1888, 243, 193), however, in a careful series of experiments, obtained by the two methods identical sulphine iodides which gave rise to identical series of double salts. At the same time, they pointed out that Krüger's method of preparation was at fault and that his substances were impure.

From the facts that conflicting results have been obtained, and that the bulk of the evidence in these researches is based upon the behaviour of certain double salts, it seemed possible that an investigation of these substances might throw some light upon the matter. The following research has therefore been undertaken, firstly, to attempt to determine the constitution of the double salts of the sulphine bases, and, secondly, to ascertain whether, by varying the methods of preparation, stereoisomeric compounds could be obtained.

In acetone or alcoholic solution, the sulphides unite with mercuric iodide to form compounds of the general formula  $R_2SHgI_2$ . These are analogous to such substances as  $R_2SI_2$ ,  $R_2SBr_2$ ,  $R_2SRI$ , &c., and their constitution must therefore be represented in a corresponding manner, that is, as containing quadrivalent sulphur: 
$$R > S < \begin{matrix} HgI \\ I \end{matrix}$$

Mercuric iodide and the alkyl iodides might be expected to react in a similar way with the mercaptans forming substances such as 
$$\begin{matrix} R & & I \\ & \diagdown & / \\ & S & \\ & / & \diagdown \\ H & & HgI \end{matrix} \quad \text{and} \quad \begin{matrix} R & & I \\ & \diagdown & / \\ & S & \\ & / & \diagdown \\ H & & R \end{matrix}$$
 These, however, do not appear as products of the reaction, and may be assumed to be unstable com-

pounds, formed at an intermediate stage, and readily splitting off hydrogen iodide as follows:



Regarded from this point of view, the acid nature of the alcohols and mercaptans appears to be dependent on the tendency of oxygen and sulphur to become quadrivalent, and since oxygen shows this tendency to a less degree than sulphur, it follows that the alcohols show weaker acid properties than the mercaptans. That this is the case is illustrated by the fact that ethyl mercaptan, dissolved in an alcoholic solution of sodium ethoxide, shows all the reactions of sodium mercaptan; for example, on treating with alkyl iodides, the sulphides are formed.

The alkyl iodides react with the mercuric iodide compounds of the sulphides to form stable yellow substances, which are found to be identical with those produced from the corresponding sulphine iodides and mercuric iodide. Accordingly, their formation must be represented as follows:

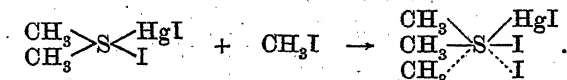


Dobbin and Masson (Trans., 1885, 47, 56) have already investigated the products of addition of the halogens to the sulphine halides, and conclude that they are not molecular compounds, but owe their formation to either sexavalent sulphur or tervalent iodine. From their stability and from the fact that the sulphine sulphates give similar compounds, these authors incline to the former hypothesis.

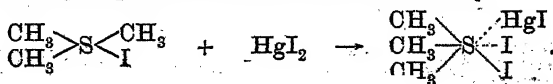
In support of this view, I have found that dimethyl sulphide bromide,  $(\text{CH}_3)_2\text{SBr}_2$ , reacts with methyl iodide to give the same substance,  $(\text{CH}_3)_3\text{SBr}_2\text{I}$ , as is produced from trimethylsulphine iodide and bromine in molecular proportion.

The following series of reactions were carried out with the object of investigating the stereochemical properties of sexavalent sulphur. As yet, only negative evidence has resulted. It has been found that the same compound of trimethylsulphine iodide with mercuric iodide is produced in the following three different ways.

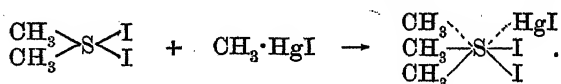
From dimethyl sulphide-mercuric iodide and methyl iodide:



From trimethylsulphine iodide and mercuric iodide:

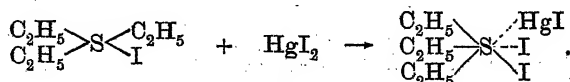


From dimethyl sulphide iodide and mercury methyl iodide:

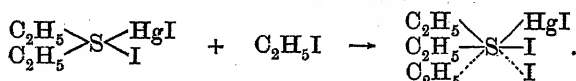


The following two reactions also give identical products.

Triethylsulphine iodide and mercuric iodide:



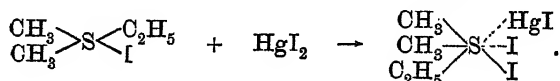
Diethyl sulphide, mercuric iodide, and ethyl iodide:



The same process has been applied to derivatives containing only two of the three alkyl groups alike.

The following reactions give identical products.

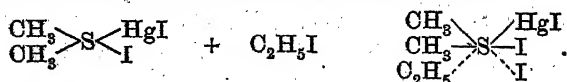
Dimethylethylsulphine iodide and mercuric iodide:



Methyl ethyl sulphide-mercuric iodide and methyl iodide:

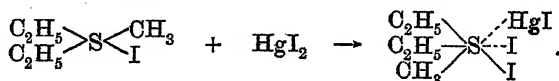


Dimethyl sulphide-mercuric iodide and ethyl iodide:

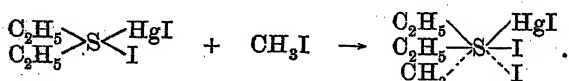


Also the same compound of diethylmethylsulphine iodide with mercuric iodide is produced by the following reactions.

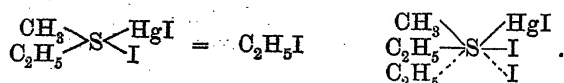
Diethylmethylsulphine iodide and mercuric iodide:



Diethyl sulphide-mercuric iodide and methyl iodide:



Methyl ethyl sulphide-mercuric iodide and ethyl iodide:



From these results, no definite conclusion can be drawn as to the relative directions of the six valencies of sulphur. Even the simplest arrangement, that in which the valencies are directed towards the six angles of an octahedron, allows of three possible isomerides in the case of  $(\text{CH}_3)_2\text{SIHgI}_2$ . Where the alkyl groups differ, the possible number becomes still larger. As, however, Wedekind (*Ber.*, 1899, 32, 517) and others have shown that quaternary ammonium compounds containing two or more small groups, such as methyl and ethyl, are not obtained in isomeric forms, and that the presence of more complex groups, as phenyl or benzyl, renders this isomerism possible, it is desirable to repeat these experiments with derivatives containing larger radicles.

It is a noteworthy feature of these reactions that the presence of mercuric iodide appears to render the addition of alkyl iodide far easier of accomplishment than is the case in its absence. Thus, for example, the action of ethyl iodide on dimethyl sulphide-mercuric iodide is complete in 10 to 15 minutes with the formation of  $(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2\text{SIHgI}_2$ , whilst, on the other hand, the production of dimethylethylsulphine iodide from ethyl iodide and dimethyl sulphide is scarcely complete in 3 days.

It is hoped, therefore, that this method of preparation will be of use in obtaining sulphines containing higher radicles and possibly those of the aromatic series, which do not appear to be readily formed by the ordinary methods.

#### EXPERIMENTAL.

##### *Action of Mercuric Iodide on Alkyl Sulphides.*

The sulphides of the fatty series dissolve mercuric iodide with slight evolution of heat and formation of the mercuric iodide-sulphides. These substances are best prepared by shaking up a warm concentrated solution of the sulphide in acetone with mercuric iodide, which dissolves, the solution acquiring a yellow colour. After filtering or decanting from excess of mercuric iodide, the solution is either left to crystallise or, if the product is very soluble, evaporated in a vacuum. These substances are yellow, unstable compounds, the lower members of the series crystallising well in long prisms. They are soluble in acetone, but only sparingly so in alcohol or ether. When exposed to the air or gently warmed, they are decomposed, leaving a residue of mercuric iodide, the same decomposition occurring when they are boiled with water or acids. Potassium hydroxide solution converts them to yellow substances, from which acids regenerate the original mercuric iodide sulphides. On account of their tendency to decompose, and the consequent difficulty in obtaining them sufficiently pure for analysis, their composition was determined as follows. A weighed quantity of

sulphide dissolved in acetone or ether was shaken with a known amount of mercuric iodide in excess. The remaining mercuric iodide was removed by filtration, washed with ether, and, after drying, weighed. Owing to the slight solubility of mercuric iodide in acetone or ether, the numbers obtained were generally a little low.

*Dimethyl sulphide-mercuric iodide*,  $(\text{CH}_3)_2\text{SHgI}_2$ , crystallises from acetone in long, yellow needles and melts at  $75^\circ$ . Estimation of the amount of mercuric iodide which entered into combination with the sulphide gave the following results:

0.183 requires 1.322  $\text{HgI}_2$ .  $\text{HgI}_2 = 87.8$ .

0.235     "      1.70  $\text{HgI}_2$ .  $\text{HgI}_2 = 87.8$ .

$\text{C}_2\text{H}_6\text{I}_2\text{SHg}$  requires  $\text{HgI}_2 = 87.9$  per cent.

*Methyl ethyl sulphide-mercuric iodide*,  $\text{CH}_3(\text{C}_2\text{H}_5)\text{SHgI}_2$ , crystallises from acetone in pale yellow prisms and melts at  $59^\circ$ . On analysis, the following result was obtained:

0.356 requires 2.166  $\text{HgI}_2$ .  $\text{HgI}_2 = 85.9$ .

$\text{C}_3\text{H}_5\text{I}_2\text{SHg}$  requires  $\text{HgI}_2 = 85.6$  per cent.

*Diethyl sulphide-mercuric iodide*,  $(\text{C}_2\text{H}_5)_2\text{SHgI}_2$ , crystallises from acetone, in which it is very soluble, in pale yellow prisms and melts at  $52^\circ$ . It was analysed by weighing the residue of mercuric iodide obtained by gently heating a known quantity to a temperature slightly above its melting point.

0.3026 gave 0.2516  $\text{HgI}_2$ .  $\text{HgI}_2 = 83.14$ .

0.5505     "      0.4565  $\text{HgI}_2$ .  $\text{HgI}_2 = 82.92$ .

$\text{C}_4\text{H}_{10}\text{I}_2\text{SHg}$  requires  $\text{HgI}_2 = 83.45$  per cent.

*Amyl sulphide-mercuric iodide*,  $(\text{C}_5\text{H}_{11})_2\text{SHgI}_2$ , is obtained as a yellow oil which easily decomposes on heating. On analysis, it gave the following result:

0.5 requires 1.24  $\text{HgI}_2$ .  $\text{HgI}_2 = 71.2$ .

$\text{C}_{10}\text{H}_{22}\text{I}_2\text{SHg}$  requires  $\text{HgI}_2 = 72.2$  per cent.

*Dibenzyl sulphide-mercuric iodide*,  $(\text{C}_7\text{H}_7)_2\text{SHgI}_2$ , is very soluble in acetone; it crystallises in pale yellow, transparent plates and melts at  $37-38^\circ$ . It is exceedingly unstable in the solid state and decomposes on being pulverised, but is more stable when in solution. On analysis, the following numbers were obtained.

1.1435 requires 2.53  $\text{HgI}_2$ .  $\text{HgI}_2 = 68.8$ .

0.926     "      2.05  $\text{HgI}_2$ .  $\text{HgI}_2 = 69.0$ .

$\text{C}_{14}\text{H}_{14}\text{I}_2\text{SHg}$  requires  $\text{HgI}_2 = 67.9$  per cent.

Of the foregoing derivatives, some are stated to have already been obtained. Loir (*Annalen*, 1858, 107, 234) claims to have prepared the dimethyl (m. p.  $67^\circ$ ) and the diethyl derivative (m. p.  $110^\circ$ ) by the

action of ethyl iodide on dimethyl sulphide-mercuric chloride and diethyl sulphide-mercuric chloride respectively, and describes them as stable yellow substances. These are evidently derivatives of sulphine bases, since, as shown below, such substances are produced from alkyl iodides and the mercuric iodide sulphides.

*Compounds of Sulphine Iodides with Mercuric Iodide. Action of Alkyl Iodides on the Mercuric Iodide Sulphides.*

The alkyl iodides dissolve the mercuric iodide sulphides, and on allowing the solutions to stand for a few minutes they become warm, gradually acquiring a bright yellow colour. Precipitation with ether yields yellow, crystalline products, identical with those produced from the corresponding sulphine iodides and mercuric iodide. These are stable, yellow, crystalline substances, and, especially in the case of the lower members of the series, can be easily obtained in large, well-defined crystals. They show a slight tendency to split off mercuric iodide, although to a far less degree than the mercuric iodide sulphides. When suspended in water in the finely divided state and boiled, only a very slight decomposition occurs. With potassium hydroxide solution, they yield a white substance soluble in acetone.

The mercury in these compounds was estimated as follows. The substance was decomposed by treatment with nitric and hydrochloric acids, and the solution evaporated to dryness. The resulting mercuric chloride was dissolved in water, and from the solution, after neutralising with sodium carbonate and then acidifying with hydrochloric acid, the mercury was precipitated as sulphide and estimated in the usual manner.

It may be noted that all the following reactions appear to take place quantitatively.

*Trimethylsulphine iodide-mercuric iodide*,  $(\text{CH}_3)_3\text{SIHgI}_2$ , was prepared in three ways.

1. The calculated quantities of trimethylsulphine iodide and mercuric iodide were shaken up with acetone. From the yellow solution, ether precipitated a crystalline substance melting at  $163^\circ$ , which, after recrystallisation from acetone, melted at  $165^\circ$ . By allowing a cold solution in acetone to evaporate spontaneously, it was deposited in large, yellow prisms often half a centimetre across.

2. Dimethyl sulphide-mercuric iodide was dissolved in an excess of methyl iodide; interaction took place with slight evolution of heat, and was complete in two minutes. On cooling, a substance separated out which melted at  $163$ — $164^\circ$ , and from the mother liquor a further quantity was obtained by precipitation with ether. After precipitating twice from acetone with ether, it melted at  $165^\circ$ .

3. The substance was also produced from dimethyl sulphide

iodide and mercury methyl iodide, but whether the reaction may be regarded as an additive one is a matter of doubt. 0.6 gram of dimethyl sulphide and 2.5 grams of iodine were dissolved in 5 c.c. of acetone and 3.4 grams of mercury methyl iodide added. In about 15 minutes, the reaction was complete, and on cooling the mixture in ice a crystalline precipitate was obtained melting at 140—145°.

After precipitating twice from acetone with ether and crystallising once from acetone, it melted at 163—164°. Together with this substance there was formed another, which may be obtained from the mother liquor; it melted at 68—70°, and on analysis showed rather a high percentage of mercury (31.05 per cent.). Analyses of the substances prepared by the above three methods were made, with the following results:

- I. 0.3686 gave 0.1289 HgS. Hg = 30.17.
- II. 0.3513 „ 0.1235 HgS. Hg = 30.29.
- III. { 0.2129 „ 0.0755 HgS. Hg = 30.56.
- 0.2410 „ 0.0855 HgS. Hg = 30.58.

$C_3H_5I_3SHg$  requires Hg = 30.39 per cent.

It is evident from these results that the substance obtained by the third method still contained a small quantity of the compound of lower melting point.

*Triethylsulphine iodide-mercuric iodide*,  $(C_2H_5)_3SIHgI_2$ , was obtained by two methods. It was found that concentrated acetone solution of trimethylsulphine iodide, when saturated with mercuric iodide and precipitated with ether, formed a yellow, crystalline substance which melted at 116°, and on analysis the following result was obtained:

0.5372 gave 0.2143 HgS. Hg = 34.38.

$(C_2H_5)_3SI_2HgI_2$  requires Hg = 34.66 per cent.

1. The following method was therefore used for the preparation of the required compound. An acetone solution of triethylsulphine iodide was divided into two equal parts, one of which was shaken with excess of mercuric iodide. After filtering, the solution was added to the second part and the whole concentrated by spontaneous evaporation. By precipitation with ether, a substance was obtained which melted at 107—108°, and after purification crystallised in bright yellow leaflets melting at 112°.

2. Diethyl sulphide-mercuric iodide was dissolved in excess of ethyl iodide and the interaction, which took place with evolution of heat, was complete in about fifteen minutes. On the addition of ether, a substance was precipitated which melted at 109—110° and after recrystallisation at 112°.



Analyses of the products of the above reactions were made, with the following results:

- I. 0.2462 gave 0.0810 HgS. Hg = 28.35.
  - II. 0.2593 „ 0.0857 HgS. Hg = 28.48.
- $C_6H_{15}I_2SHg$  requires Hg = 28.57 per cent.

*Dimethylethylsulphine iodide-mercuric iodide*,  $(CH_3)_2(C_2H_5)SIH_2I_2$ , was prepared by three methods.

1. Dimethylethylsulphine iodide was dissolved in acetone and the calculated quantity of mercuric iodide added. From the solution, ether precipitated a substance which melted at  $85^\circ$  and, when pure, crystallised from acetone in long, yellow prisms melting at  $87^\circ$ .

2. Dimethyl sulphide-mercuric iodide was dissolved in excess of ethyl iodide, and after standing for 12 to 15 minutes, the interaction was complete. From the solution, a yellow, crystalline substance melting at  $85^\circ$  was precipitated by ether, and this, when recrystallised from acetone, formed long prisms which melted at  $86.5^\circ$ .

3. An excess of methyl iodide was added to methyl ethyl sulphide-mercuric iodide, and the interaction, which took place immediately with slight evolution of heat, was complete in about 2 minutes. On adding ether, a yellow substance melting at  $78-79^\circ$  was obtained, which, after reprecipitating twice from acetone, melted at  $87^\circ$ .

When the mixture of methyl iodide and methyl ethyl sulphide-mercuric iodide was allowed to stand longer than about 15 minutes, an impure product was obtained. In one experiment, the mixture was allowed to stand for 2 hours, and a crystalline substance was then obtained which melted at  $160-161^\circ$ , and was evidently the trimethyl derivative. The solution contained a mixture of other substances.

Analyses of the products of the above three reactions were made, with the following results:

- I. 0.43 „ gave 0.1483 HgS. Hg = 29.72.
  - II. 0.5981 „ 0.2050 HgS. Hg = 29.54.
  - III. 0.4512 „ 0.1545 HgS. Hg = 29.51.
- $C_4H_{11}I_2SHg$  requires Hg = 29.76 per cent.

*Methyldiethylsulphine iodide-mercuric iodide*,  $CH_3(C_2H_5)_2SIH_2I_2$ , was also obtained in three ways.

1. 2.5 grams of methyldiethylsulphine iodide were dissolved in acetone and 4.9 grams of mercuric iodide added. From the solution, ether precipitated a yellow, crystalline substance which melted at  $64-65^\circ$ , and after reprecipitating twice from acetone by ether, at  $67^\circ$ ; its acetone solution, when allowed to evaporate spontaneously, deposited large, transparent, yellow plates.

2. A concentrated solution of 6 grams of diethyl sulphide-mercuric

iodide was treated with an excess (3 grams) of methyl iodide. After standing for 3 minutes, the solution was precipitated with ether, giving 5 grams of a yellow, crystalline compound melting at 63—64°. After purification, the product melted at 67°, and could be easily obtained in large plates.

3. Methyl ethyl sulphide-mercuric iodide was dissolved in ethyl iodide, and in a quarter of an hour the reaction was complete. The product obtained by precipitation melted at 60—62°, but when purified by solution in acetone and precipitation with ether, at 66·5°.

When the substances prepared by these methods were analysed, the following numbers were obtained :

- I. 0·6543 gave 0·2213 HgS. Hg = 29·15.  
 II. 0·3950 „ 0·1330 HgS. Hg = 29·02.  
 III. 0·3051 „ 0·1027 HgS. Hg = 29·01.  
 $C_5H_{13}I_3SHg$  requires Hg = 29·15 per cent.

It appears, then, so far as these experiments go, that no isomerism exists among the compounds which the sulphine iodides form with mercuric iodide. Although the supposition that these substances contain sexavalent sulphur allows of its possibility, isomerism does not follow as a necessary consequence, for, as already pointed out in the introduction, similar isomerism among the nitrogen compounds is non-existent in the lower members of the series, and only appears when the nitrogen is united to larger and more complex radicles.

In connection with this work, attempts have been made to resolve methyl ethyl thetine,  $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > S < \begin{matrix} CH_2 \cdot CO \\ O \end{matrix}$ , into optically active components, but without success. It was found that any attempts to prepare a strychnine or cinchonine salt of the hydrobromide of the thetine,  $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > S < \begin{matrix} CH_2 \cdot CO_2H \\ Br \end{matrix}$ , resulted in the formation of its anhydride and the hydrobromide of the active base. Silver malate and the thetine hydrobromide gave similar results. Experiments were also made with *Penicillium glaucum*, but it was found that only a very slight growth of the mould took place after standing for some weeks with a 2 per cent. solution of the anhydride, the solution being inactive.

In conclusion, I wish to express my thanks to Professor Ramsay for the interest he has taken in the work described in this paper, and the help he has afforded me in carrying it out.





Seinem lieben Prof. Thorpe  
mit herzlichsten Grüßen von  
Hans zu Hans Victor Meyer

## VICTOR MEYER MEMORIAL LECTURE.

(DELIVERED ON FEBRUARY 8th, 1900).

By T. E. THORPE, Ph.D., D.Sc., LL.D., F.R.S., President of the  
Chemical Society.

By the untimely death of Victor Meyer, on August 8th, 1897, under circumstances of peculiar sadness, and at the comparatively early age of forty-nine, our sister Society in Berlin lost her President of the year, and, at the same moment, we were deprived of one of the most brilliant of that band of eminent men whom we distinguish as our Honorary Foreign Members. The Council have deemed it fitting that the attempt should be made to put on record our appreciation of the remarkable services Victor Meyer rendered to the science which he cultivated, during the all too short period of his activity, with such striking assiduity and success. As a friend of nearly thirty years' standing, and as one who worked, literally, side by side with him in the famous laboratory which he lived to direct, and died whilst directing, I have charged myself with the execution of this duty.

Of Meyer's early life—that is, of the period before I first knew him at Heidelberg as a girlish-looking, bright-eyed youth, quick of movement and active in thought, ready and fluent of speech, full of zeal, and intensely interested in the higher work of the place—I know little, beyond that he was born in Berlin and was the son of a calico manufacturer.\* Once, in the course of some discussion on the characteristic differences in the school training of English and German lads, he made reference to his own experiences in the gymnasium, from which I gathered that his inclination towards science was in nowise shaped by what he saw or heard in early youth. Nor, so far as can be determined, was there anything in his home life which inclined him to take to chemistry. In the case of many who have become eminent in physical science—and doubtless also in the case of more who have not—their first love has sprung from the passion of experimenting. But at this time Meyer, apparently, had neither the opportunity nor the desire to make experiments. Indeed, the home atmosphere tended to make him literary or artistic. There can be no doubt that he owed to this environment, and more especially to the example and precept of his mother, herself a woman of considerable intellectual power, certain strongly marked features of character which

\* The date of his birth was September 8th, 1848.

are not usually associated with men of science. According to his friends Liebermann and Jacobson, his own wish was to become an actor, and that he would have succeeded in such a profession is highly probable. He had, indeed, all the natural gifts of the born actor—dramatic sense, emotional power, a fine voice, an impressive manner, and a handsome presence. When he became a teacher of chemistry, these attributes were turned to good account. His early love of declamation, combined with his elocutionary ability, eventually made him one of the most striking and effective lecturers in Germany. The traditions of the University lecture-theatre no doubt exercised their restraining influence, but Meyer was too much under the sway of his artistic temperament and too impatient of conventionality to repress altogether his natural bent. Moreover, he was not insensible to the effect he created, or unmindful of the influence he gained, when, to use the common phrase, he “let himself go,” and by his trenchant, impressive language, and the brilliancy of his illustration, communicated something of his own enthusiasm to even the most listless of back-bench men. This power of exposition was quickly perceived, and no doubt its early recognition served to bring him the more speedily to the front.

At Heidelberg, as in many other centres of chemical instruction, there was a small Chemical Society, composed of the Extraordinary Professors, the Privat-docenten, and assistants, together with the senior or more active students in the various laboratories who were elected into it by favour of the teachers. In my time it numbered amongst its members Erlenmeyer, Ladenburg, Horstmann, Ludwig, Cohen (the mineralogist), Rose, and Emmerling. Its president was Bunsen, and the occasions on which he took the chair were the red-letter days of the session. We invariably sent him home happy, his pockets filled with all the good champagne corks we could collect. The formal business of the Society—if formal it can be called—was preceded by an *Abendessen*, and if not accompanied, at least succeeded, by a considerable manifestation of “das gemüthliche Element.” No man was more popular at these gatherings than Meyer. His nimble mind and retentive memory, his gift of ready speech, his sense of humour and genial manner combined to make it pleasant to listen to him no matter whether he was, in accordance with the rules of the Society, called upon to give an account of some work which had just been published, or whether he was discussing and criticising a communication from a fellow member. From time to time we had reports of the condition of such investigations as were in progress in the Heidelberg laboratories, or of which the results were to appear in the forthcoming issue of the *Annalen*, for, at the period of which I write, the *Berichte* was a thin and puny publication, hardly out of its swaddling clothes, and with little sign of the

vitality which has since enabled it to assimilate practically the whole outcome of German chemical activity.

Of his own laboratory work, we had nothing from Meyer, for there was little or nothing at the time to be told. He had entered the University in the autumn of 1865, when barely seventeen years of age, and apparently with no very definite conception of a career. Suddenly he elected to study chemistry, and attached himself to Bunsen with the idea of ultimately becoming a teacher. It is not improbable that his choice was in a measure determined by the circumstance that he had attended some of Hofmann's lectures in Berlin in the preceding summer, and had thus been influenced by that great teacher, then in the fulness of his intellectual vigour. Those were the palmy days of Heidelberg—the days of Bunsen, Kopp, Kirchhoff, Helmholtz—and Meyer came under the spell of them all. His progress as a student was exceptionally rapid, and the brilliant manner in which he gained his doctorate—without the adventitious aid of a thesis—strongly impressed the whole philosophical faculty. Bunsen, especially, was greatly struck with the power and promise of the young Jew, then one of the youngest students in the University, and soon selected him as one of his assistants. It was in this capacity that I first made the acquaintance of Meyer. Bunsen for some years previously had been engaged in the examination of the mineral waters of South Germany, and Meyer at the time I entered the Heidelberg laboratory was acting as water analyst. However great the disciplinary value of such work might be (and no one who has practised Bunsen's method of water analysis, with its system of check and control, can doubt that it is one of the most rigorous quantitative exercises possible), I fear it was not altogether congenial to the active mind of the young assistant, who was yearning to try his 'prentice hand at original research. Accordingly, towards the end of 1868 he threw up the position, and entered Baeyer's little laboratory at the Gewerbeakademie in Berlin. Although in a sense overshadowed by the more magnificently appointed University laboratories of Hofmann in the Georgenstrasse, and of Kekulé in Bonn, both at that time comparatively new, the modest laboratory of the Gewerbeakademie, with its twenty workers, was already one of the most famous schools of organic chemistry in Europe. Baeyer himself had recently published his brilliant investigation of mellitic acid; and Graebe, at first alone, and subsequently in conjunction with Liebermann and with Caro, was at work on those remarkable series of inquiries which served to establish the true chemical nature and relationships of alizarin, and led eventually, with the independent collaboration of Perkin, to its artificial production on a commercial

scale. I well remember the interest and excitement which these discoveries created in Germany: they unquestionably gave an enormous impetus to the study of organic chemistry and attracted eager aspirants for chemical fame from all parts of the world, quickened, no doubt, by the perception of the rich promise of material benefit thus suddenly opened up. Heidelberg at that period was pre-eminently a school of inorganic chemistry: organic chemistry was represented by Delffs and was mainly studied by prospective apothecaries. Erlenmeyer had been called to the Polytechnic at Munich, and the influence of Kekulé's teaching was as yet hardly felt by any of the Privat-docenten.

Baeyer quickly recognised the power and ability of his pupil, and to Baeyer was undoubtedly due the impulse which started him on his career. As a "Vorgerückter" he attended no more lectures, and thus it happened that he who became one of the greatest organic chemists of his time never followed a course on organic chemistry. Shortly after his entrance into the laboratory, he began the series of half-dozen investigations which characterised his activity during his three years' stay in Berlin. His first paper, published in the *Berichte*, was a note on the action of trimethylamine upon monochlorhydrin, which substances form a basic condensation product, the chloride and the gold salt of which he described (*Ber.*, 1869, 2, 186). This was quickly followed by a short paper on diethyl thiodicarbonate,  $S(CO_2Et)_2$ , which he obtained by the action of ethyl chloroformate upon sodium sulphide (*Ber.*, 1869, 2, 297).

A far more ambitious production appeared in the following year, dealing with the constitution of the disubstituted benzenes (*Annalen*, 1870, 156, 265). In this memoir, Meyer described a new method of introducing a carboxyl group into the molecule of aromatic compounds, no matter whether the substance already contained a carboxyl group or not. This was effected by the action of sodium formate upon the potassium salt of the aromatic sulpho-acid.

Of the acids prepared synthetically by this method, isophthalic acid was the most important on theoretical grounds, as its production under these conditions led to a revision of the views then held with respect to the orientation of the radicles in the "ortho" and "meta" (salicylic) series. Isophthalic acid had been shown by Baeyer to be a 1:3-derivative. "Ortho"-sulphobenzoic acid, obtained from benzoic acid, was thought to have its radicles in contiguous positions. Meyer's experiments showed that isophthalic acid was the only dicarboxylic acid formed from the sulpho-acid by interaction with a formate, whence he argued that "ortho"-sulphobenzoic acid, and the chloro-, bromo-, nitro-, amido-, and hydroxy-benzoic acids corre-



sponding with it in constitution, must, like the isophthalic acid, be 1:3-derivatives. It followed that the "meta" (salicylic) series of compounds are the 1:2-compounds.

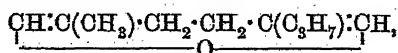
The main facts of this paper have long since taken their place in the history of our knowledge of aromatic compounds, but the memoir has an especial interest as being Meyer's first excursus into the realm of chemical theory. In a subsequent extension of the work, in conjunction with Ador (*Annalen*, 1871, 159, 1), he showed that in sulphanilic acid the substituent groups  $\text{SO}_3\text{H}$  and  $\text{NH}_2$  were in the 1:4 positions. The phenolsulphonic acid from sulphanilic acid he proved to be identical with Kekulé's paraphenolsulphonic acid, and hence to have the position 1:4. Potassium monobromobenzoate fused with sodium formate yields isophthalic acid; hence this bromobenzoic acid belongs to the 1:3 series. At the conclusion of their memoir, the authors gave a list of the disubstituted derivatives of benzene then known, arranged in columns according to whether the second substituent element or radicle is attached to the second, third, or fourth carbon atom, as deduced from the experimental evidence put forward. Their views as to the orientation of the substances there named, except in the case of the dihydroxybenzenes, have not been materially modified by subsequent inquiry.

Pending the publication of this work, Meyer essayed to solve that *arcana* of aromatic chemistry, the constitution of camphor (*Ber.*, 1870, 3, 116). He sought to show in the first place that camphoric acid is a dicarboxylic acid,  $\text{C}_8\text{H}_{14}(\text{CO}_2\text{H})_2$ . Since camphor yields, by the action of dehydrants, an homologue of benzene, namely, cymene, he reasoned that it must contain the benzene nucleus, and hence the remaining four carbon atoms must exist in the side-chains. But by the oxidation of camphor to camphoric acid, the side-chains apparently are not attacked; the action would seem to be on two of the carbon atoms in the benzene ring. The carboxyl groups cannot be attached to one and the same carbon atom, otherwise camphor would not yield an homologue of benzene by abstraction of water. It would follow therefore that, in all probability, camphor ought to have the constitution expressed by one or other of the following formulæ:

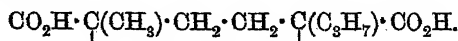
- (1)  $\text{COH} \cdot \text{C}_8\text{H}_{14} \cdot \text{CH}$ .
- (2)  $\text{C}(\text{OH}) \cdot \text{C}_8\text{H}_{14} \cdot \text{CH}$ .
- (3)  $\text{CH} \cdot \text{C}_8\text{H}_{14} \cdot \text{CH}$ .

The first, or aldehydic, formula, suggested by Berthelot, was practically disproved by the work of Fittig and Tollens. The second formula, which contains the hydroxyl group, was rendered improbable by

Berthelot, and the improbability was further strengthened by Meyer, who found that acetic chloride was without action on camphor. The third formula then would seem of the three to be the most probable. The constitution of the group  $C_8H_{14}$  can only be inferred from that of the camphor cymene. This, as shown by Fittig and his pupils, is probably for the most part methylpropylbenzene.\* Hence camphor would appear to have the constitution



and camphoric acid



Borneol would be  $\text{CH}(\text{OH}) \cdot \text{C}_8\text{H}_{14} \cdot \text{CH}_2$ . These views have now only an historical interest. All that is certain in them is that Meyer's conception of camphoric acid as a dicarboxylic acid is correct. The work of Claisen and Manasse has rendered it practically certain, as long surmised, that camphor has the grouping  $C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{CO} \end{smallmatrix}$ . It has, however, required the labour of a generation of workers, and the accumulation of a literature which, as regards its bulk, is without a parallel in any other department of chemistry, to unravel the true relations of camphoric acid to camphor, and hence to get an insight into the constitution of a substance which has been known in Europe and prized as a medicine since the twelfth century.

Meyer acquired some experience in tuition, even in the early Heidelberg days, as a "coach," and in Berlin he added to his means, which were slender enough, by similar work. His success as a teacher induced Baeyer to recommend him to Fehling, who sought assistance, especially in modern organic chemistry and in laboratory teaching, in connection with his duties at the Stuttgart Polytechnic. His departure from Berlin was a great loss to the little circle in the Gewerbeakademie, where his high spirits and geniality made him universally popular. He was an omnivorous reader and the power of his memory was astonishing, so much so that on his leaving, Baeyer exclaimed "Jetzt werden wir ja wieder die Literatur nachschlagen müssen."

He remained in the Württemberg capital barely a year. How he came to leave it has already been told by Professor Liebermann. Johannes Wislicenus had just been called from the Zürich Polytechnic to Würzburg, and the President of the school, Kappeler, was engaged in searching for a successor. He came to Stuttgart and, unknown to

\* Widman (*Ber.*, 1891, 24, 450) subsequently proved that cymene is methylisopropylbenzene, but this does not affect Victor Meyer's argument.

Meyer, attended one of his lectures. Although Kappeler, as he himself relates, knew little of chemistry, he was so struck with Meyer's power of lucid and stimulating exposition that the decision to invite him to Zürich was immediately made. At the close of the lecture, he communicated to the unsuspecting young teacher his idea, expressing, however, his fear that in comparison with his future students he might prove to be still too young. As Meyer laughingly promised to do his best, day by day, to repair this fault, the invitation was given, and thus, when barely 24 years of age, he found himself Ordinarius and Director of the chemical laboratory of the Zürich Polytechnic.

The Zürich Polytechnic has enjoyed a succession of distinguished teachers, and Meyer worthily sustained and, indeed, greatly extended the fame of its chemical chair. He was now in possession of a well equipped laboratory and surrounded by eager, active students, stimulated and encouraged by the enthusiasm of a teacher as active and eager, and, it may be added, as high-spirited as themselves. The thirteen years of Meyer's stay at Zürich constitute the most fruitful and the most brilliant period of his career: before its close, he had brought himself within the foremost rank of contemporary investigators. Some idea of his wonderful power of work, and of the stimulus he gave to others, may be gleaned from the fact that during that period the Zürich laboratory, under Meyer's direction, gave close upon 130 papers and memoirs to chemical literature. It is, of course, impossible here to do more than indicate, in the briefest possible outline, the outcome and significance of the more important of them.

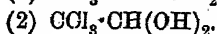
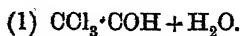
During his short stay at Stuttgart he sent some half dozen papers to the *Berichte*, some of them in continuation of work which had occupied him in Berlin. The chief of these were put together in a memoir, in conjunction with Stüber, on the aromatic amines, which appeared in 1873 (*Annalen*, 1873, 165, 161). The main object of the work was to gain further evidence in favour of Meyer's view, that in the case of the chloro-, bromo-, iodo-, and nitro-derivatives of aromatic amines, obtained by direct substitution, it is always the hydrogen immediately contiguous to the amido-group which is replaced, or, in other words, that the  $\text{NH}_2$  group exercises an attractive influence on the substituent. It was assumed by Kekulé that Riche and Bérard's dibromaniline, obtained by the reduction of dibromonitrobenzene, was identical with the dibromaniline from acetanilide. Meyer and Stüber proved that such was not the case. It was found that Riche and Bérard's dibromaniline yields, or is derived from, a *liquid* dibromobenzene, which boils at  $219.4^\circ$ , and remains liquid at  $-28^\circ$ . Riese had previously obtained a liquid dibromobenzene boiling at  $224^\circ$  and crystallising below  $-1^\circ$ . All the three possible dibromobenzenes were thus made known. Meyer's

surmise that the new dibromobenzene was the 1:3 variety has since been established. The authors also made known the existence of a new tribromobenzene melting at  $119^{\circ}$ , the symmetric or 1:3:5-derivative. The isomerism of the liquid dibromobenzenes was subsequently conclusively demonstrated (*Ber.*, 1874, 7, 1560) by the crystallographic examination of their mononitro-derivatives by Groth and Bodewig.

In this connection may be mentioned a short paper, in conjunction with Wurster, "On some derivatives of solid Dibromobenzene" (*Annalen*, 1874, 172, 57). In the attempt to prepare a nitrated phenylenediamine by acting upon dibromonitrobenzene with alcoholic ammonia, in the same manner that Walker and Zincke obtained nitraniline from monobromonitrobenzene, they found that only a moiety of the bromine could be displaced, the resultant product being a new substance, bromonitraniline, in which the  $\text{NO}_2$  group is next to the  $\text{NH}_2$  group. By converting this substance into bromophenylenediamine, the two  $\text{NH}_2$  groups would be in close proximity; on debrominating this compound, the resulting phenylenediamine was found to be identical with that discovered by Griess (m. p.  $99^{\circ}$ ), whose surmise that the  $\text{NH}_2$  groups were united to contiguous carbon atoms was confirmed.

Meyer began also an inquiry on the chemical nature of chloral hydrate, a substance which, in consequence of Liebreich's discovery of its anæsthetic action, had by that time become of considerable industrial importance, and was readily procurable. By the action of acetic chloride upon chloral hydrate, tetrachlorethyl acetate,  $\text{CCl}_3\cdot\text{CHCl}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ , is obtained, identical with the product formed by the condensation of chloral and acetic chloride, or by the action of acetic chloride on acetaldehyde. Chloral alcoholate with acetic chloride yields  $\text{CCl}_3\cdot\text{CH}\begin{matrix} \text{OC}_2\text{H}_5 \\ \text{O}\cdot\text{CO}\cdot\text{CH}_3 \end{matrix}$ , indicating that the alcoholate, as already shown by Henry on other chemical grounds, is the ethyl ether of trichlorethylidene glycol. By dissolving chloral hydrate in glacial acetic acid, Meyer obtained a white, crystalline substance, melting at  $80^{\circ}$ , which he regarded as isomeric with ordinary chloral hydrate (m. p.  $55^{\circ}$ ).

The chloral hydrates may have respectively the constitution



It is not proved, however, that they are not polymeric (*Annalen*, 1874, 171, 65). It is possible that the substance thus obtained is identical with the uniaxial form observed by Pope which slowly changes into the biaxial modification stable at ordinary temperatures (*Trans.*, 1899, 75, 458). Meyer does not definitely

decide which of the two formulæ represents the constitution of ordinary chloral hydrate, but he inclines to regard it as trichlorethylidene glycol, which Perkin's observations on its magnetic rotation definitely indicate that it is.

Wallach's observation of the conversion of chloral into dichloroacetic acid was shown by Meyer to be in accordance with a general property of aldehydes in alkaline solutions to take up the elements of water, one molecule of aldehyde being thereby reduced, whilst another is oxidised.

Meyer, in conjunction with his pupil Haffter, devised a very simple and rapid method of estimating the actual quantity of pure chloral in the commercial product, founded on the fact that chloral hydrate is rapidly decomposed by an aqueous solution of an alkali into chloroform and an alkaline formate (*Ber.*, 1873, 6, 600).

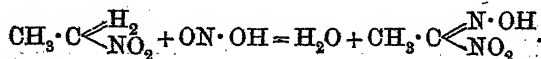
Although Meyer's papers up to this time had amply demonstrated his power of investigation, and afforded to critics like Kekulé and Baeyer abundant proof of the clearness and keenness of his vision, he had hitherto worked upon somewhat conventional lines. His memoir "On the Nitro-compounds of the Fatty Series" (*Annalen*, 1874, 171, 1), which appeared shortly after his removal from Stuttgart to Zürich, at once stamped him as an original investigator of a very high order. In anticipation that two series of alkyl nitrites would be found to exist, denoted in the methyl series by  $\text{CH}_3\cdot\text{NO}_2$  and  $\text{CH}_3\cdot\text{O}\cdot\text{NO}$ , Meyer, whilst still at Stuttgart, had studied the action of amyl iodide upon silver nitrite and had obtained a colourless liquid, having the ordinary smell of amyl compounds, boiling between  $150^\circ$  and  $160^\circ$ , which on analysis was found to have the composition  $\text{C}_5\text{H}_{11}\text{NO}_2$ . Hence it was isomeric with amyl nitrite, a yellow liquid of a peculiar, disagreeable smell, which boils at  $99^\circ$ . To the new compound Meyer gave the name of nitropentane. The reaction was found to be general. He now entered upon an elaborate investigation of the nitro-compounds of the alkyl series and their derivatives, and of questions incidental to the main subject, which, in conjunction with his pupils, among whom may be mentioned Stüber, Rilliet, Chojański, Wurster, Constam, Janny, Lecco, Locher, Tcherniac, Ceresole, Müller, Demuth, Keppler, and Züblin, continued to occupy him at intervals for upwards of twenty years.

One peculiarity which distinguishes aromatic from aliphatic compounds consists in the ease with which 'nitration,'—that is, the replacement of hydrogen by the group  $\text{NO}_2$  with the elimination of water—may be effected in the first-named substances. A reaction analogous to that by which nitrobenzene is formed from benzene was scarcely known among fatty compounds, the most familiar instance being the production of chloropicrin by the action of strong nitric

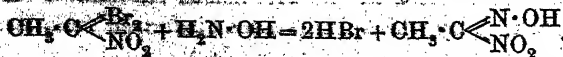
acid upon chloroform. The constitutional difference between the nitroparaffins, as the new group came to be called, and the alkyl nitrites consisted in the fact that, in the first-named substances, the  $\text{NO}_2$  group is directly connected with a carbon atom, as in nitrobenzene, whereas in the alkyl nitrites the  $\text{NO}$  group is intermediately linked with the hydrocarbon radicle by means of oxygen. The alkyl nitrites are true esters capable of being resolved into alcohols and nitrous acid by the hydrolytic action of alkalis or acids. The nitroparaffins, on the other hand, are incapable of hydrolysis. By reduction, they yield alkyl hydroxylamines and then the corresponding amine. By reduction, however, the alkyl nitrites lose their nitrogen and form the corresponding alcohol.

Meyer's view that the nitroparaffins were veritable nitro-compounds was not at once accepted. Geuther, and subsequently Götting, assumed that nitroethane was acetamidoxide,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}_2\text{O}$ , whilst Kissel regarded it as acethydroxylamine,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}(\text{OH})$ . It is true, as found by Meyer, that nitroethane, under the hydrolytic influence of strong acids, splits up into hydroxylamine and acetic acid, but since phosphoric chloride is without action upon nitroethane, an hydroxyl group must be assumed to be absent. As for Geuther's view of the constitution of these substances, Meyer had little difficulty in showing that it wholly failed to explain all their known reactions.

The general characteristics of the nitroparaffins, namely, the power of forming salts possessed by the primary and secondary compounds, the absence of this power in the tertiary series, together with the remarkable differences in the behaviour of bromine, and of the action of acids upon the primary and secondary nitroparaffins, were carefully studied by Meyer and his pupils. He found that when a solution of a primary nitroparaffin in potash is mixed with an alkaline nitrite and treated with sulphuric acid, the liquid acquires a blood-red colour which disappears on the further addition of acid. On shaking the whole with ether, there is obtained a solution of a new acid, known as a nitrolic acid, of the general formula  $\text{C}_n\text{H}_{2n+1}\cdot\text{C}\begin{smallmatrix} \nearrow \text{N}\cdot\text{OH} \\ \searrow \text{NO}_2 \end{smallmatrix}$ . In the case of nitroethane, the formation of the ethylnitrolic acid may be represented as follows:



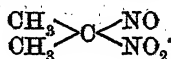
That such is the constitution of ethylnitrolic acid is indicated by its formation by the action of hydroxylamine on dibromonitroethane,



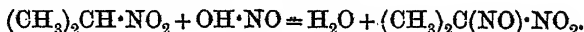
The nitrolic acids are colourless, sweet-tasting substances of a strong

acid reaction, readily soluble in water, and for the most part easily crystallisable. In alkaline solution, they give an intense blood-red coloration and form characteristic precipitates with salts of the heavy metals. They slowly decompose on standing, and on heating are quickly resolved into the corresponding fatty acid, nitrogen, and nitrogen dioxide. On treating the nitrolic acids with sodium amalgam, substances known as azaurolic acids are formed. They are strongly coloured, sparingly soluble substances, and differ from the corresponding nitrolic acid by containing two atoms of oxygen less. The best known member of the series is ethylazaurolic acid,  $C_2H_4N_2O$ , or more probably  $C_4H_8N_4O_2$ . On heating, it yields, together with formation of nitrous oxide and water, ethylleucazone,  $C_4H_7N_3O$ , a substance possessing both acid and basic properties, and in its general characteristics resembling an amido-acid.

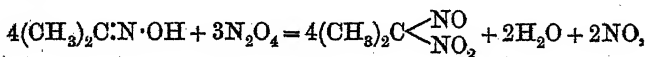
The secondary nitroparaffins, when treated with nascent nitrous acid, behave quite differently from the primary compounds. On adding sulphuric acid to the mixed solutions, a deep blue colour is produced and insoluble substances are formed, isomeric with the nitrolic acids, but which have no acid character. They were called by Meyer pseudo-nitroles, and have been regarded as nitroso-nitro-compounds.



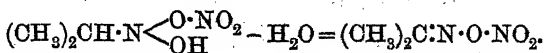
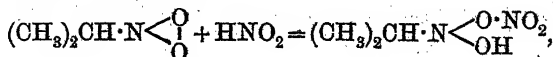
Their formation may be thus represented



Scholl subsequently discovered that these substances may be obtained by the action of nitrogen peroxide upon the ketoximes: thus with acetoxime:



a mode of formation which, as Meyer pointed out, indicated that they may be regarded as the nitrates of the oximes,  $(\text{CH}_3)_2\text{C}:\text{N}\cdot\text{O}\cdot\text{NO}_2$ . Their formation from the secondary nitro-compounds may be supposed to occur in the following phases:

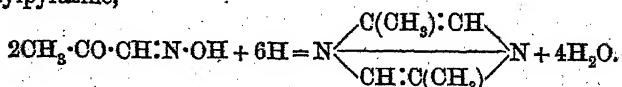


Meyer was inclined to give the preference to the latter view of their constitution, as it is generally very doubtful whether compounds containing a nitroso-group (NO) directly linked to a carbon atom are capable of existence.

Tertiary nitro-compounds are unchanged by the action of nascent nitrous acid.

Meyer pointed out how the characteristic colour reactions afforded by the behaviour of nitrous acid with the primary and secondary nitro-paraffins, and its inability to act upon the tertiary compounds, offered a ready means of distinguishing primary, secondary, and tertiary alcohol radicles. The iodide to be tested is distilled with silver nitrite, the distillate shaken with a solution of potassium nitrite in strong potash, diluted with water, and mixed drop by drop with dilute sulphuric acid. If the liquid acquires a red colour (formation of nitrolic acid) which disappears with excess of acid and reappears on the addition of alkali, we are dealing with a primary radicle: should the liquid give a blue colour (formation of pseudonitrole) soluble in chloroform, the compound is derived from a secondary alcohol radicle; the non-formation of colour indicates a tertiary radicle. The test ceases to be of much practical value beyond the 5 carbon series (compare Meyer and Jacobson, *Lehrbuch der Organischen Chemie*, 1893, 253, *et seq.*).

The same line of inquiry was extended to the other main groups of aliphatic substances, and resulted in the discovery of new types of compounds. Thus, by the reduction of the isonitrosoketones and the isonitrosoacetoacetic esters, Meyer, in conjunction with Treadwell, obtained a series of volatile bases having apparently the generic formula  $C_nH_{2n-4}N_2$ , which they termed ketines and subsequently aldines. This group of substances is now generally known as the azines, and the substance first described by Meyer and Treadwell is dimethylpyrazine,

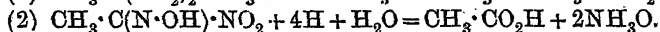
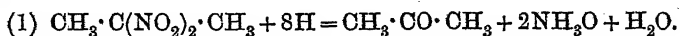


Meyer had the faculty of keeping more irons hot at a time than any man of his period. Although much of his thought and energy was directed in the first years of his sojourn in Zürich to the development of the new field of inquiry which his discovery of the nitroparaffins opened out, he continued his work on aromatic compounds, partly in defending positions he had already secured, and partly in breaking new ground. In the latter connection, reference may be made to his discovery, with Michler, of diazoxybenzoic acid, and to the new class of azo-compounds which he described in conjunction with Ambühl.

A point of some little interest at the time (1875) was his discovery that hydroxylamine and nitrous acid together yield nitrous oxide and water,  $NH_2O + NO_2H = 2H_2O + N_2O$ , in the same manner that nitrous acid and ammonia form nitrogen and water. The production of nitrous oxide by mixing together concentrated aqueous solutions of



hydroxylamine sulphate and sodium nitrite constitutes a neat and striking lecture experiment. He also showed, with Locher, that hydroxylamine may be obtained by a number of new reactions, as, for example, by acting on dinitropropane or ethylnitrolic acid with tin and dilute hydrochloric acid, when, in the one case, the amine is liberated in conjunction with acetone, and, in the other, together with acetic acid.



These reactions showed that the rule, hitherto regarded as universally true, that nascent hydrogen reduces nitroxyl to amidogen, has its exceptions.

But perhaps the most important of Meyer's discoveries at this period was that of the oximes. He had observed that dibromonitroethane, under the action of hydroxylamine, passes into ethylnitrolic acid, and he anticipated that the analogous nitrosoacetone would be formed in like manner from unsymmetrical dichloracetone. Experiment showed, however, that the chlorine in dichloracetone was replaced by a hydroxylamine rest, whilst the ketonic oxygen was replaced by the oximido-group, forming a compound termed by Meyer acetoximic acid, but now known as methylglyoxime,  $\text{CH}_3 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH}(\text{N} \cdot \text{OH})$ . The fact that hydroxylamine would thus react upon carbonyl oxygen induced him, in conjunction with Janny, to study the action of this reagent upon ordinary ketones and aldehydes, and thus led to the discovery of the ketoximes and the aldoximes. This discovery has a two-fold significance. The reaction not only serves to indicate the existence of carbonyl oxygen in compounds, and hence is of value as a mode of determining constitutional problems, but it brought into existence a number of substances yielding derivatives of considerable interest. Further, it is not too much to say that the stereochemistry of nitrogen takes its rise from the discovery of the oximes.

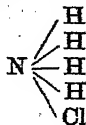
With Janny, he likewise obtained  $\alpha$ -nitrosopropionic acid by the action of hydroxylamine on pyroracemic acid, a reaction which is almost quantitative and capable of being used as a test for pyroracemic acid.

Lossen discovered hydroxylamine as far back as 1865. Although it was quickly recognised as an exceedingly reactive substance, its use was greatly curtailed by the difficulty and expense of preparing it in quantity. Much of it, prior to 1883, was obtained by Dumreicher's process, namely, by reducing ethyl nitrate by means of stannous chloride and hydrochloric acid. Meyer showed how the irksomeness of the method, entailed by the necessity of removing the tin by sulphuretted hydrogen, and of dealing with the large volume of liquid produced,

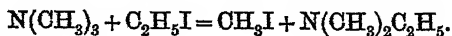
might be materially lightened, and considerable quantities of hydroxylamine salts were made by the modified process in the Zürich laboratory.

The position which hydroxylamine occupies between ammonia and nitric acid, which at that time were held to be the main nitrogenous foods of plants, as well as its great chemical activity when compared with the inertness of the other substances, seemed to Meyer to point to a possible formation of hydroxylamine within the plant, and to its playing an important part in the assimilation of starch and in the formation of albuminoids. In conjunction with Schulze, he therefore made comparative experiments on the action of hydroxylamine, ammoniacal salts, and nitrates upon plants, when it was quickly found that hydroxylamine acted as a poison to vegetable organisms. Meyer, however, points out that it may still be possible that hydroxylamine may be formed in transition products, and yet act as a poison when taken up by the roots, just as peptone behaves as a poison when injected into the veins of animals.

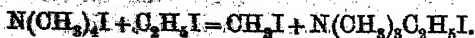
Reference may here be made to Meyer's attempts to elucidate the constitution of ammonium salts. It was found that the dimethyldiethylammonium iodide, obtained by the action of ethyl iodide on dimethylamine, is identical with that produced by acting with methyl iodide on diethylamine, and no difference can be detected in the character of their salts. As the substances, although identical, were obtained by different reactions, it was inferred that they could not be 'molecular' compounds, that is, combinations of a tertiary base with an alkyl haloid, but must contain pentavalent nitrogen, whence, by analogy, ammonium chloride would be



This assumption is only sound on the supposition that, in the formation of the salts, no change had taken place in the position of the alcohol radicles. The main conclusion would be invalidated if, for example, ethyl iodide, when reacting on trimethylamine, did not combine directly with it but was decomposed, as Lossen had suggested, as follows:



To ascertain if such an interchange occurred, Meyer, in conjunction with Lecco (*Annalen*, 1876, 180, 173), studied the action of ethyl iodide upon tetramethylammonium iodide. If Lossen's contention were sound, the reaction should be



No action, however, was found to occur either with ethyl or methyl iodide alone at any temperature up to  $180^{\circ}$ , or in presence of methyl alcohol or water. Ladenburg and Struve tested Meyer's conclusion by making similar experiments with benzyl iodide and triethylamine, and with ethyl iodide and benzyldiethylamine, and were disposed to regard the resultant compounds as isomeric, although closely alike in most of their properties. On repeating the observations, Meyer found that no difference existed; the substances prepared in the two ways were absolutely identical.

Suggestive and fruitful in ideas as Meyer was, he was seldom at a loss in devising means to put them to the test of trial. In many of his mental characteristics not unlike Davy, as an experimentalist, he had all Davy's resourcefulness with far more than his patience.

As I knew him in Heidelberg, he was an excellent manipulator; still his temperament would never have permitted him to better the example of the great master under whom he was trained. We could all look on and marvel at the patient, concentrated power with which Bunsen would devise, elaborate, and perfect some new form of apparatus, or some new method of analysis. The first steps were very simple—so simple indeed that it was frequently impossible to divine their ultimate purpose. It was from such small beginnings that we obtained the whole process of gasometric analysis, the burner, the photometer, the various voltaic batteries, the spectroscope, the filter-pump, the ice-calorimeter, the flame reactions, &c. Before Bunsen gave a piece of apparatus to the chemical world, he left it practically perfect; the striving after perfection was a veritable passion with him, and numerous were the forms or modifications through which the apparatus or the method passed before he rested satisfied with it. Although Meyer's genius was of a different order, the influence of the Heidelberg training is to be recognised in the various forms of laboratory apparatus with which his name is connected. Chief among these are his modes of determining vapour densities. The elegant modification of Gay Lussac's method introduced by Hofmann left nothing to be desired in the case of comparatively volatile substances unacted upon by mercury, but many bodies were known, and their number was being rapidly increased, in which this method was inapplicable. Meyer accordingly, in 1876, devised his displacement method (*Ber.*, 1876, 9, 1216). This in principle was similar to the method suggested by W. Marshall Watts as far back as 1867, from which it differed in that Wood's metal—an alloy of bismuth, lead, tin, and cadmium, melting below  $70^{\circ}$ —replaced the mercury, and that the volatilisation was effected at the temperature of boiling sulphur, that is, at  $444^{\circ}$ . This process allowed of the determination of the vapour density of many substances which could

be vaporised at temperatures below the boiling point of sulphur, and compounds like diphenyl, methylantracene, triphenylamine, paradibromobenzene, and paradiphenylbenzene, had their vapour densities ascertained for the first time by means of it.

The method was further modified in the following year (*Ber.*, 1877, 10, 2068), mercury being used instead of Wood's metal and the vapours of boiling water, aniline, ethyl or amyl benzoate or diphenylamine—depending on the temperature required—were employed as a bath instead of sulphur vapour.

The "Luftverdrängung Methode"—the simple and extremely convenient process—which will for all time be associated with the name of Victor Meyer, was devised in 1877 (*Ber.*, 1877, 11, 1867). The apparatus is now one of the commonest articles of laboratory furniture, and it is not too much to say that, thanks to the ease with which the whole operation may be carried out, more vapour densities have been determined by its aid than by any other means.

The apparatus is usually constructed of glass, but by making it of glazed porcelain, determinations can be effected at very high temperatures. Except for special reasons, neither the temperature of the heated bulb nor its volume need be known: all that is required is that the temperature should be sufficiently high to gasify the substance under examination. A variety of liquids—water, xylene, aniline, ethyl benzoate, amyl benzoate, diphenylamine—depending on the temperature needed to effect complete vaporisation, may be used as media for heating the bulb. For temperatures exceeding 300°, a bath of molten lead may be employed, the glass bulb of the apparatus being coated, as suggested by Watson Smith and Davis, with a moderately thick film of soot before immersion in the bath so as to diminish the risk of fracture.

Mr. Watson Smith, who was with Meyer at Zürich, and who has kindly sent me some reminiscences of him at this period, writes: "It was somewhat singular that just as Victor Meyer, with Carl Meyer (no relation), had completed their vapour density apparatus for bodies of very high boiling point, I had just obtained in the pure state specimens of the three isomeric dinaphthyls, all of which urgently awaited the determination of their vapour densities. They were the first new high boiling substances with which the apparatus and method were tried. Victor Meyer was immensely pleased and interested with this circumstance, and we practically all three worked the determination together, the results amply proving the reliability and accuracy of the new method. Of course in these cases the lead bath was used" (compare *Trans.*, 1879, 35, 226; 1880, 37, 491).

The molecular weights of a number of substances were quickly ascertained by this method, for example, phosphorus pentasulphide, indium chloride, cuprous chloride, stannous chloride, arsenious oxide,

antimonous oxide, cadmium bromide, &c. Volatilised in an atmosphere of hydrogen chloride, ferrous chloride yielded values between  $\text{FeCl}_2$  and  $\text{Fe}_2\text{Cl}_4$ . Ferric chloride at no temperature showed a vapour density corresponding with  $\text{Fe}_2\text{Cl}_6$ , whilst at  $750^\circ$  and  $1077^\circ$ , its molecule would seem to be  $\text{FeCl}_3$ . Potassium iodide at  $1320^\circ$  in an atmosphere of nitrogen had a density corresponding with KI. Arsenic and phosphorus at a white heat had densities approaching the values for  $\text{As}_2$  and  $\text{P}_2$ , whilst zinc at  $1400^\circ$ , and bismuth at  $1700^\circ$ , were found to be monatomic, and thallium at  $1700^\circ$  diatomic.

In 1879, the two Meyers, Victor and Carl, astonished the chemical world by announcing (*Ber.*, 1879, 12, 1426), as the result of determinations of their vapour densities at high temperatures, that the halogens were capable of undergoing dissociation or possibly decomposition. As regards chlorine, this announcement at once threatened to re-open a question which had been regarded by most people as practically settled since July 12th, 1810, when Davy read to the Royal Society his classical memoir on oxymuriatic acid. Davy, it is true, had never stated that chlorine was an element in the absolute sense of that term. What he inferred was that it was a substance which "has not as yet been decomposed," and therefore is "elementary as far as our knowledge extends." The very name chlorine, which he suggested, inculcated this view. "To call a body which is not known to contain oxygen and which cannot contain muriatic acid, oxymuriatic acid, is contrary to the principles of that nomenclature in which it is adopted. . . . After consulting some of the most eminent philosophers in this country, it has been judged most proper to suggest a name founded upon one of its obvious and characteristic properties—its colour, and to call it *chlorine*, or *chloric gas*. Should it hereafter be discovered to be compound, and even to contain oxygen, this name can imply no error, and cannot necessarily require a change."

Had chlorine then been 'decomposed'? Did it contain oxygen? Were Berzelius and Murray right after all? Was there such an entity as murium? The pages of the popular scientific periodicals of the time show how these questions agitated the minds of chemists. The indications of the spectroscope were advanced as confirmatory of Meyer's results, and there was much exercise of 'the intelligent anticipation of events before they occur' which occasioned him some annoyance at the time. However sanguine he might be that he had decomposed chlorine, and however freely he might talk with his colleagues, he never committed himself in print to any statement of the kind. To begin with, the amount of oxygen he had obtained was very small, and there was uncertainty as to the action of the chlorine upon the silica or alumina of the

porcelain at the high temperature, and whether the materials employed were wholly free from moisture. I have it, on the authority of Professor Lunge, whose knowledge was derived from daily intercourse with him, that Meyer himself refused to consider the fact as established until he had worked in an apparatus made of material devoid of oxygen, and to this end he obtained a special grant from the Zürich authorities to defray the cost of a vessel of platinum.

Meanwhile Meyer's observations on chlorine were repeated, and their validity impugned by Crafts (*Compt. rend.*, 1880, 90, 183 *et seq.*) who found, by a modification of Meyer's method, that the gas, even at the highest temperature of the Perrot furnace, showed no change indicative of dissociation or decomposition. Meyer, in conjunction with Züblin, at once repeated Crafts' determinations on pre-formed chlorine and confirmed their accuracy.

As regards bromine and iodine, however, the observers were in substantial agreement.

Thus with iodine :

Victor Meyer.			Crafts and Meier.		
Temp.	Density.	$D'/D$ .	Temp.	Density.	$D'/D$ .
450°	8.85	—	445°	8.74	—
586	8.72	0.99	830—880	8.07	0.92
342	6.76	0.77	1020—1050	7.01	0.80
1030	5.75	0.66	1275	5.82	0.66
1570	5.70	0.65	1390	5.28	0.60

Naumann showed from these results, on the assumption that the molecule  $I_2$  splits up into two atoms  $I+I$ , that the course of the dissociation is in accordance with the result required by the mechanical theory of gases, namely, that the increments of decomposition corresponding to equal differences of temperature increase gradually from the temperature at which dissociation begins up to that at which 50 per cent. of the vapour is decomposed, and then decrease in a similar manner up to that temperature at which dissociation is complete.

In conjunction with Langer, Meyer greatly extended these observations, and subsequently published them as a monograph, entitled "Pyrochemische Untersuchungen" (Braunschweig: Vieweg u. Sohn, 1885).

As regards bromine, they found that the gas, when sufficiently diluted with air, had a normal density, namely, 5.52 even at the ordinary temperature, and no sensible change occurred up to 900° even when diluted with eleven times its volume of nitrogen. At 1200°, the density had diminished to 4.3 on dilution with five volumes of nitrogen. At a white heat, the density of the diluted bromine fell to 3.6. Experiments at higher temperatures were not possible,

as at above  $1600^{\circ}$  the platinum apparatus is rapidly attacked by both bromine and chlorine.

The alteration in density of bromine vapour at high temperatures has recently been studied by Dr. Perman and Mr. Atkinson, who have found that no sensible diminution occurs up to about  $750^{\circ}$  at atmospheric pressure, at which point dissociation becomes just appreciable, especially at low pressures, and gradually increases with increasing temperature (*Proc. Roy. Soc.*, 1900, 66, 10).

In the case of chlorine, it was found by Meyer and Langer that no analogous change occurred below  $1200^{\circ}$ , no matter whether pure or highly diluted chlorine was employed. At  $1400^{\circ}$ , however, the density of the diluted chlorine fell from the normal value 2.45 to 2.02.

Similar observations with carbon monoxide seemed to show that at  $1690^{\circ}$  this gas is partially decomposed into carbon dioxide and carbon,  $2CO = C + CO_2$ . Carbon dioxide itself experiences no change in density at this temperature in a platinum apparatus, although when passed through a porcelain tube filled with broken pieces of porcelain it undergoes dissociation, as already shown by Deville. This phenomenon may be connected with the remarkable observation of Menschutkin and Konowaloff that dissociable vapours are far more rapidly broken up in presence of asbestos, or pieces of glass, or even of the roughened sides of glass, than when the interior of the glass vessel is perfectly smooth.

Nitrous oxide, heated in a porcelain tube, is entirely resolved into oxygen and nitrogen at  $900^{\circ}$ , and in a platinum tube at  $1690^{\circ}$ . Nitric oxide remains unchanged up to  $1200^{\circ}$ ; at  $1690^{\circ}$ , it is completely decomposed into its elements. Hydrogen chloride also appears to be partially, whilst sulphuretted hydrogen is entirely, decomposed at the latter temperature. Cyanogen has a normal density up to  $800^{\circ}$ ; at  $1200^{\circ}$ , it suffers decomposition.

Meyer made his pyrochemical investigations under very unfavourable conditions. The magnificent chemical institution which Zürich now possesses was not then built. The old laboratory was a low building to the east of the main block of the Polytechnicum, and the only room which could be spared for the purpose was so small that, in spite of the best ventilation possible, the temperature not unfrequently rose to  $50^{\circ}$ . Moreover, both he and his assistants suffered greatly from the strenuous ardour with which the work was carried on, and he himself eventually broke down under the strain of it. I saw him in Zürich in the autumn of this year (1879), and was surprised and shocked to notice, although it was at the end of the vacation, how nervous and jaded he seemed. I believe the distressing insomnia from which he suffered at times throughout the rest of his life began at about this period. In reference to this time, Mr. Watson Smith writes: "Meyer had a most excitable

mind and was a tremendous worker. His assistant, Carl Meyer, told me that on several occasions he was so overworked, not by compulsion, but through the mere influence of Meyer's presence, his mental power, and enthusiasm, that he came very near committing suicide during the fits of depression following exhaustion after long-continued spells of work."

Pyrochemical problems continued to interest Meyer to the end, and he was quick to take advantage of any hint which seemed to promise the possibility of their solution. In a lecture before the Naturforscher Versammlung in Heidelberg, he regretted that the lack of vessels of sufficiently refractory material prevented him from working at the higher limits of temperature even then attainable. "There can be no doubt," he said, "that new and undreamt-of discoveries will manifest themselves—that a new chemistry will disclose itself, when we are furnished with vessels that will enable us to work at temperatures at which water can no longer exist, and at which oxy-hydrogen gas becomes an unflammable mixture."

Shortly before his death, he returned to the subject with new apparatus made of a platinum-iridium alloy capable of withstanding a far higher temperature than pure platinum, and he was in hopes of being able to construct vessels of magnesia which would allow of the application of temperatures over 2000°.

Meyer, at the time he announced his discovery of the dissociation of the halogens, was thirty-one years of age. He was now on the flood-tide of his prosperity. His published work had shown him to be an investigator of uncommon power and originality, and students flocked to him from all parts, to participate in the pioneering work which his astonishing energy and enthusiasm opened out. In its triumphs it was indeed a time of "joyous yesterdays and confident to-morrows." He was happily married to the friend of his youth, Fraülein Hedwig Davidson, whose 'Verlobungstag' was the very day on which he received his call to Zürich. What she was to Meyer only those who were privileged to know his home circle can fully realise.

Meyer's first great grief came to him with the death of his eldest daughter, and in 1882 he lost his friend Wilhelm Weith, Professor of Chemistry in the University. How close and intimate was their friendship was evident to all who frequented the meetings of the Zürich Chemische Gesellschaft, where the two professors were generally to be found seated side by side at the head of the table; it is reflected too in the obituary notice of his colleague which Meyer wrote for the *Berichte*.

In the autumn of 1882, Meyer was requested to undertake the delivery of the series of University lectures on benzene derivatives



which had been interrupted by Weith's death. I have already attempted to indicate what Meyer was as a teacher. No one could possibly take greater pains in the preparation of his lectures, or study more to make them instructive and interesting. It is generally supposed that organic chemistry does not lend itself to effective lecture illustration. Such was not the case when Meyer had to teach it. "I well recollect," writes Mr. Watson Smith, "that the word most frequently used in Zürich in defining the opinions of Victor Meyer's students of his lectures was 'brilliant!'" Another of our Fellows, Mr. John I. Watts, who attended his course in 1879-80, writes:—

"What particularly struck me about his lectures was their finished style. He made fairly constant use of notes, speaking with great rapidity. Yet his treatment of the subject was very clear, and his language perfect. The experiments were always well prepared and exceptionally successful. Indeed, his lectures were most popular, and both at his work and outside the Polytechnic there was no professor who was more respected and admired by all students than Victor Meyer. Young, handsome, well-dressed—for a German professor, with a quick wit and a genial manner, he was a welcome addition to any gathering. When, in 1881, he had a 'call' to Aachen and elected to remain at Zürich, the students treated him to a torchlight procession and a grand 'Kommers.' Meyer watched the 'Fackelzug' of over 1000 students from a balcony, and later, sitting as the honoured guest in a still greater throng, he seemed indeed a happy man."

Similar testimony is given by Dr. Sudborough, who was with him in Heidelberg, and who writes:—

"As a lecturer, Meyer was clear, concise, and extremely lucid, and his delivery was easy and natural. His lectures were given by the aid of carefully written notes, and were fully illustrated by experiments, the table being always crowded with apparatus both in the organic and inorganic lectures. It was very rare indeed for an experiment to fail; this was firstly due to Meyer's own dexterity as a manipulator, and also to the care which was bestowed upon the preparation of the experiments."

It was in the course of these lectures on benzene derivatives that Meyer came upon what is perhaps the most brilliant of all his discoveries—that of thiophen. How he lighted upon it is well known, but the story bears repetition. He desired to show his class the so-called indophenin reaction of Baeyer, at that time held to be indicative of benzene, but to his astonishment not a trace of the characteristic blue colour made its appearance, although, as was his wont, he had rehearsed the experiment just prior to the lecture. It appeared that his assistant, Sandmeyer—himself one of Meyer's 'discoveries'—had handed to him a sample of the benzene made in the lecture course by heating benzoic acid with lime, and at once drew his attention to the fact that the rehearsal had been made with the ordinary laboratory supply—

the *Benzol purissim. crystallisatum* of the dealers, and, of course, derived from coal-tar. Meyer, at the moment, was so fully occupied that he might well have put aside the incident, or have given no immediate heed to its significance. But that was not his way. Fortune scatters her chances indifferently, and every man may have his share, but it is not given to each to perceive when he is favoured, or to know when to grasp "the skirts of happy chance." Madame de Staël once said that a most interesting book might be written on the important consequences which spring from little differences, and it was the little difference that riveted itself on Meyer's mind. He at once began the investigation of the cause. All kinds of benzene to be found in Zürich were tested, and it was soon definitely established that it was only coal-tar benzene that gave the indophenin reaction. Meyer's first idea was that it might be occasioned by an isomeric—a second benzene found in coal-tar. Within less than a month he had ascertained that the reaction was due to some sulphuretted product accompanying coal-tar benzene, and that Baeyer's indophenin was probably a sulphur compound. Meyer's action was characteristic of him. Before communicating with Baeyer, he carefully repeated his experiments, and only when all ground for doubt was removed did he inform his friend of his observations and of the inferences he had formed. Baeyer at once sent him a specimen of his indophenin, and the fact that it actually was a sulphuretted compound was then established. Meyer found that coal-tar benzene, after repeated shaking with oil of vitriol, no longer reacted with isatin, and hence he determined to search among the sulphonic acids so formed for the reactive substance. By distilling the product obtained by shaking 10 litres of benzene with oil of vitriol, he obtained a few cubic centimetres of a clear, thin, mobile liquid containing sulphur, which boiled at about  $83^{\circ}$  and remained liquid in a freezing mixture of ice and salt. It gave a most intense reaction for indophenin. The amount of the new substance present in coal-tar benzene was very small, at most not more than 0.5 per cent.

Thanks to the co-operation of his friends, Messrs. Bindschedler, Busch and Co., of Basle, he was enabled to repeat this experiment on a large scale, as much as 250 litres of coal-tar benzene being operated upon at a time, and the sulphonic acids converted into the lead salts, which were then mixed with sal ammoniac and distilled. The crude product, which contained about 28 per cent. of sulphur, was found to react strongly with bromine, forming a heavy, colourless, highly refractive liquid, boiling at  $211^{\circ}$ , greatly resembling dibromobenzene, but showing on analysis the composition  $C_6H_2Br_2S$ . The new compound was the dibromo-substitution product of a substance which

Meyer was at first inclined to call *thianthren*, then *thiophan*, next *thiol*, and lastly *thiophen*, to denote that it was a sulphur-containing substance giving derivatives analogous to those of phenyl.

In the early part of the following June, that is, within about six months of his first observation, he had obtained a considerable quantity of thiophen, and was in a position to show to the Swiss Naturforscher Versammlung, which met during that summer in Zürich, that its chemistry was hardly less extensive than that of benzene itself. Thus it was that a chance observation—the observation of a little difference—added a new section to organic chemistry.

It would be quite impossible within the limits at my disposal to show how this section was developed by Meyer and his pupils. In 1888, he published, in the form of a monograph, dedicated to his friend and patron, President Kappeler, “dem hochherzigen Förderer wissenschaftlicher Bestrebungen,” an account of its condition at that time (*Die Thiophengruppe*. Braunschweig: Vieweg u. Sohn), from which it appears that during the preceding five years no fewer than 106 contributions to its history had been made from his own laboratory, and some 40 from those of others. How fertile the field still continues may be gleaned from the circumstance that upwards of 50 papers on the same subject have since made their appearance in various journals.

Meyer's restless energy had now begun to react most seriously upon his general health. At times he was almost prostrated by nervous exhaustion; he had frequent spells of insomnia, and his friends viewed with alarm the signs of physical decay which now set in, in spite of the occasional holidays, mainly among the Alps, which he gave himself. In 1884, he again broke down, and although at the moment he was immersed, with his colleague Lunge, in the plans for the new chemical laboratory of the Polytechnic in which, as he states, he had hoped ultimately to resume his pyrochemical labours under more favourable conditions, he was obliged to relinquish, for a time, all idea of work, and towards the end of the year was ordered away to the Riviera, where he wintered. In the following spring, he received a 'call' to Göttingen as the successor of Hübner. This he eventually decided to accept, and entered upon his duties there in the summer session of 1885.

He was not able, as he had hoped, to take leave of his Zürich students at the time, but what they thought of him—with what affection and respect he was regarded—was seen in the terms of the Address they sent to him on the occasion of his opening lecture at Göttingen. It was seen, too, in the way he was received by them during a visit to Zürich some months later, on the occasion of the seventieth birthday of his friend Kappeler. Professor Goldschmidt,

who was present, thus describes the scene: "I see him even now before me as he spoke to the students at the 'Kommers' in the evening. The 'Zürcher Polytechnikers' have, as a rule, but little opportunity of knowing the professors outside their special faculty, and have, therefore, but little interest in those who are not their own teachers. As Victor Meyer's slender form appeared on the platform, and as his bright blue eyes glanced round the assembly, there broke forth a shout of welcome from all—engineers, machinists, architects, as well as from his old students the chemists—to be ended in a whirlwind of applause at the close of a speech, sparkling and witty as ever."

With renewed health and vigour, he now set about the plans for the new laboratory which the authorities had decreed should adorn the 'Georgia-Augusta,' for Wöhler's old place no longer sufficed to contain the chemical workers which Göttingen had now to receive. Whilst it was being erected, he continued his pyrochemical work, and his investigation of the thiophen derivatives, and began with Paul Jacobson the admirable "Text-book of Organic Chemistry," which, in the critical selection and arrangement of its material, is still unsurpassed.

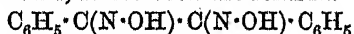
With Auwers, he resumed the study of benzil and its derivatives which he had begun with Wittenberg and Goldschmidt. With Münchmeyer, he began the study of the behaviour of phenylhydrazine towards various groups of oxygen compounds, and he sent a short paper to the *Berichte* on thiodiglycol compounds, and on an easy method of preparing  $\beta$ -iodopropionic acid from glycerol. With Demuth, he undertook the investigation of the sulphuranes, a group of disulphides of the general formula  $C_2H_5 \cdot S \cdot C_2H_4 \cdot SR$ . Other papers were on the density of nitric oxide, which showed no evidence of association or molecular duplication even at  $-100^\circ$ ; on isophthalaldehyde; on the negative nature of the phenyl group; and on isodibromosuccinic acid.

It was characteristic of his receptivity that Meyer should be among the earliest workers in Germany to perceive the value of Raoult's method of ascertaining molecular weights; it was first used in the Göttingen laboratory to determine the molecular weight of some derivatives of benzil which yielded two series of isomeric compounds, both series having the same constitution, in the ordinary sense, but which were yet distinct from one another and yielded different derivatives.

Other papers of this period were on the thio-derivatives of deoxybenzoin and its analogues (desaurins), and, with Riecke, on the carbon atom and valency. The latter paper is of interest as an example of Meyer's "scientific use of the imagination," and may

be studied in connection with an earlier paper in 1876 (*Annalen*, 1876, 180, 192) on the same subject, as showing how he grafted the theoretical conceptions of van't Hoff upon the teaching of Kekulé. According to Meyer, the carbon atom is surrounded by an ethereal shell which, in the case of an isolated atom, has a spherical form; the atom itself is the carrier of the specific affinities, the surface of the shell is the seat of the valencies; each affinity is determined by the existence of two opposite electrical poles, which are situated at the end-points of a straight line small in comparison with the diameter of the ethereal shell. Such a system of two electric poles is called a double- or di-pole. The four valencies of a carbon atom would be represented by four such di-poles, the middle points of which are situated on the surface of the ethereal shell, but freely movable within it. The di-poles themselves can rotate freely round their middle point. The carbon atom has a greater attraction for positive than for negative electricity, and the positive pole of a valency is slightly stronger than the negative pole. This hypothesis explains why the four valencies take up the position of a regular tetrahedron; why they can be diverted from this position; why the valencies of one and the same carbon atom cannot combine together, whilst the valencies of different carbon atoms can do so; why there are two kinds of single-binding, one stable, and the other allowing free rotation; and lastly, why free rotation ceases in cases of double- or treble-binding (*Ber.*, 1888, 21, 946; compare *Abstr.*, 1888, 549).

Stereochemical questions—we owe the phrase to Meyer—were indeed at this time occupying much of his thought. In a paper with Auwers (*Ber.*, 1888, 21, 784), he pointed out that the existence of the two isomeric dioximes of benzil, discovered by him in conjunction with Goldschmidt, would, if for both the formula



were established, be in direct contradiction to the hypothesis of van't Hoff that two carbon atoms united by a single affinity are free to rotate, the axis of rotation being the bond of union, and that isomerism is only possible for those substances of the type  $\text{C} \equiv \text{C}$ , which cannot, by rotation round the common axis, be converted into the same form. The two dioximes were carefully compared as regards their melting points, solubilities in water, alcohol, ether, or acetic acid, and the conditions under which the  $\alpha$ -form is converted into the  $\beta$ -modification were ascertained. To further remove all doubt as to the possibility of merely physical isomerism, and to prove that the oximes are not only different from one another, but yield different derivatives reconvertible into their respective oximes, the propionic and isobutyric derivatives were prepared and compared. The result showed that the dioximes were of identical chemical composition, and

hence it appeared that van't Hoff's hypothesis must be so altered as to admit of cases in which free rotation round the axis cannot take place, as otherwise no explanation of the isomerism of the  $\alpha$ - and  $\beta$ -dioximes is possible (compare Abstr., 1888, 597).

He subsequently showed how the work of Bethmann, Graebe, and Baeyer confirmed these views. Wislicenus' theory as to the free rotation of singly-bound carbon atoms would appear to be limited to certain cases; absolutely free rotation is probably possible only when the substituting atoms or groups are identical; where, as is the case in the majority of compounds, the atoms or groups are not identical, there will be some definite position of equilibrium; only in cases where the substituting atoms or groups are equally negative will there be several positions of equilibrium (*Ber.*, 1890, 23, 2079; Abstr., 1890, 1083).

Meyer's perspicacity and critical insight are well illustrated in a lecture which he gave to the German Chemical Society in 1890 "On the Results and Aims of Stereochemical Research." It is of interest to the student as giving a fairly complete historical account of the development of space formulæ, and more especially for its criticism of the work of Baeyer and Wislicenus on the stereochemical formulæ of single-, double-, and treble-linked carbon compounds, and of the stereochemical conceptions of Hantzsch and Werner in the case of nitrogen compounds.

With regard to the assumption that the nitrogen atom may be represented as a tetrahedron, and that the isomerism of the benzaldoximes may be similar to that of fumaric and maleic acids, it is pointed out that the structure of the oximes is in all probability not identical. Two isomeric forms of each of the unsymmetrical oximes of the formula  $\text{OH}-\text{N}:\text{CXY}$  are indicated by the hypothesis of Hantzsch and Werner, but they do not appear to exist. If the tetrahedral representation of the nitrogen atom were tenable, we should have to assume that substituted ammonias can exist in the

isomeric forms  $\text{N} \begin{smallmatrix} \text{H} \\ \swarrow \\ a \\ \searrow \\ b \end{smallmatrix}$  and  $\text{N} \begin{smallmatrix} \text{H} \\ \swarrow \\ b \\ \searrow \\ a \end{smallmatrix}$ , but such bodies are not known.

We must therefore assume that in ammonia the hydrogen atoms are placed symmetrically with regard to the nitrogen atom, and this can only find expression in a plane formula (*Ber.*, 1890, 23, 567; compare Abstr., 1890, 719).

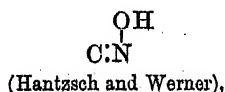
Reference may be made here to the short paper on isomeric oximes of unsymmetrical ketones and the configuration of hydroxylamine, in conjunction with Anvers (*Ber.*, 1890, 23, 2403), in which the authors advance further evidence that the isomerism of the oximes cannot depend upon structural dissimilarity, but must be sought for in the

nature of the hydroxylamine group. Assuming the correctness of the theories of van't Hoff and Wislicenus regarding the arrangement of atoms in space, the combined effect of the attraction of the nitrogen and oxygen on the hydroxylic hydrogen of hydroxylamine would cause it to be in a plane different from that occupied by the remaining atoms in the molecule. This hypothesis suffices to explain all observed facts:

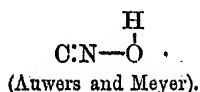
unsymmetrical oximes would therefore exist in two forms,  $\overset{a}{\text{C}}:\text{N} \cdot \overset{\text{H}}{\underset{b}{\text{O}}}$  and

$\overset{a}{\text{C}}:\text{N} \cdot \overset{\text{H}}{\underset{b}{\text{O}}}$ . The difference between this theory and that of Hantzsch and

Werner is shown by the two formulæ,



and



The formation of an oxime by the action of nitrous acid is readily accounted for on the ground that it is a substituted hydroxylamine; moreover, the fact that no case of geometrical isomerism has ever been observed in the azo-, azoxy-, and imido-compounds tells in favour of this theory (compare Abstr., 1890, 1263).

To this period belongs also the work on the azines; on deoxybenzoin; on the aromatic nitriles; on tetramethylsuccinic acid; and on the oximes of phenanthraquinone.

Meyer was not destined to remain long in Göttingen. The new laboratory was barely finished, when, in 1889, he received a 'call' to Heidelberg. Bunsen, full of years as of honours—the Nestor of Chemistry, as his friends were wont to call him—had expressed a wish to retire, and of all his many students there was none, he said, whom he wished more to take his place than he who, twenty-one years before, had worked with him in the modest little room of some four or five places, which had constituted his private laboratory. To Heidelberg accordingly Meyer went, with the coveted title of Geheimrath, and the promise of a new and enlarged laboratory. Although only forty years of age, he was now, so far as worldly position was concerned, at the summit of his career; he had returned to his Alma Mater and the rest of his days were to be given to her service.

During his four years' stay in Göttingen he had in great measure recovered his health and with it the elasticity of his active, buoyant temperament. I saw him in Heidelberg in the spring of 1891, when he was busy with the enlargement of the old laboratory, and it was

with a glance of pride—a pardonable pride—that he pointed out the places where he and I had worked with ‘Papa’ Bunsen,

‘So kindly modest, all accomplished, wise,’

in the corner place near the window, towering above both of us. It was strange, too, to hear the sound of children’s voices and their laughter; and the bustle of servants in what were formerly the silent, half-deserted rooms overlooking the Wrede-platz; and stranger still to me was it, as we together called upon Bunsen, sitting solitarily in his rooms overlooking the Bunsen-strasse, to behold the meeting and to listen to the greeting of these two men—the memory of whose names and fame Heidelberg will cherish so long as Heidelberg exists. To all of us life has its dramas, and in some of these the incidents are as moving as those ever conjured up by playwright or poet.

This was the last occasion on which I saw Meyer. How well I remember it! He was as bright, as active, as mentally vigorous as of old, although it was but too obvious that his physical strength was not the equal of his nervous energy.

Meyer’s earliest experimental work at Heidelberg was mainly concerned with the continuation of investigations begun at Göttingen. But he was perpetually breaking new ground or seeking to clear up doubtful points in ground already partially explored.

The classical labours of Frankland on zinc ethyl might be thought to have definitely established the chemistry of that substance, but even on such a comparatively simple matter as the action of oxygen on zinc ethyl there was room for still further inquiry. The white compound obtained by Frankland, as the result of the oxidation of zinc ethyl, was regarded by him as a mixture of zinc oxide, ethoxide, and acetate. It was found, however, by Meyer and Demuth to contain no acetate, but to be mainly composed of a peroxide,  $\text{ZnEt}\cdot\text{O}\cdot\text{OEt}$ , as proved by its power of liberating iodine from potassium iodide. The explosive character of the substance is thus explained. Zinc ethoxide, in fact, does not appear to have been prepared (*Ber.*, 1890, 23, 394).

In conjunction with a number of his pupils—Krause, Freyer, Askenasy, and others—Meyer in 1891 began the investigation of a subject already associated with the name of his predecessor, namely, on the conditions determining both the gradual and the explosive combustion of gaseous mixtures. Although a considerable amount of experimental work was done, the results obtained, curious and interesting as they were in some particulars, led to no very definite general conclusions.

It was found that the temperature at which combination occurred



varied with the nature of the vessel, and depended upon whether the gases were confined or not. Ignition takes place at a lower temperature when the mixture is in a closed vessel than when passing freely through an open tube. If, however, an open vessel containing the mixture is heated suddenly, explosion takes place at the lower temperature. In the cases of gradual union, no relation between time and amount of combination could be perceived. As showing the influence of the nature of the surface, it was found that, when the bulbs were silvered inside, the union of oxygen and hydrogen was rapidly effected at a temperature of about  $200^{\circ}$ , whereas in an unsilvered bulb the gaseous mixture had to be heated to above  $530^{\circ}$  before any sensible amount of water was produced. The principal quantitative results are embodied in the following table in which the mixture did not explode at the lower temperature in each column, but did so at the higher :

Equivalent mixtures.	Free current.	Closed bulbs.
Hydrogen, oxygen .....	650—730°	530—606°
Methane, oxygen .....	650—730	606—650
Ethane, oxygen .....	606—650	530—606
Ethylene, oxygen .....	606—650	530—606
Carbon monoxide, oxygen .....	650—730	650—730
Hydrogen sulphide, oxygen .....	315—320	250—270
Hydrogen, chlorine .....	430—440	240—270

In a subsequent paper with Münch (*Ber.*, 1893, 26, 2421), the temperatures of explosion of gaseous mixtures were determined by placing the vessel containing the gases inside the bulb of an air thermometer immersed in a metal bath. The mixture of a gas with the amount of oxygen theoretically necessary for its complete combustion was passed through a fine tube to the bottom of the internal vessel, and lighted as it issued from the mouth of the exit tube. At a certain temperature, the flame ran down the tube and the contents of the vessel exploded. This temperature—the temperature of explosion—was determined by displacing the air contained in the air thermometer by means of hydrogen chloride, collecting it over water, and measuring it. In 38 experiments with a mixture of hydrogen and oxygen (pure electrolytic gas), the temperature of explosion varied from  $620^{\circ}$  to  $680^{\circ}$ , being about  $650^{\circ}$  in mean. The temperature is not affected by variations in the rapidity with which the gaseous mixture enters the glass vessel, or by the presence of fragments of glass or sand. In presence of platinum, the gases combine quietly, and if the glass vessel is very small no explosion occurs. The temperatures of explosion of a number of aliphatic hydro-

carbons, mixed with equivalent amounts of oxygen, were then determined as follows:

Methane .....	656—678°	Propane .....	545—548
Ethane .....	605—622	Propylene ...	497—511
Ethylene .....	577—590	<i>iso</i> Butane ...	545—550
Acetylene ...	509—515	<i>iso</i> Butylene...	537—548
Coal-gas with 3 times its volume of oxygen ...		647—649	

It would thus appear that the temperature of explosion falls as the number of the carbon atoms in the molecule increases; that it is probably lower for primary than for corresponding secondary hydrocarbons; and is less for hydrocarbons containing a double bond than for those containing only single bonds, and still less for those containing a triple bond (compare Abstr., 1894, ii, 11).

Mention may here be made of the work done, in conjunction with Bodenstein, on the decomposition of gaseous hydrogen iodide by heat. This gas was selected for the reason that the action of heat upon it is reversible, and hence it might be expected that the establishment of a condition of equilibrium will be in no way influenced by the many disturbing circumstances which were found to occur in the case of other gaseous mixtures.

Combination of hydrogen and iodine vapour takes place even at 444° (b. p. of sulphur), and the hydrogen iodide formed is far more stable, at all events in the dark, than has hitherto been supposed. It is, however, very sensitive to light. In bulbs which were exposed for 10 days to direct sunshine, 58 per cent. of the gas was decomposed, and when exposed throughout the summer, practically the whole of the gas is resolved into its constituents. Experiments on the relation of the amount of decomposition to temperature gave the following results:

Temperature of boiling	Relative amount of HI decomposed, as determined	
	By decomposition.	By direct union.
Sulphur .....	444°	0·2150      0·2104
Retene .....	394	0·1957      —
Mercury .....	350	0·1731      0·1738

At 310° (b. p. of diphenylamine) the relative amount of HI decomposed was 0·1669, instead of 0·1550 as calculated from the above numbers. The difference between the observed and calculated results is due to the circumstance that the heat of formation of hydrogen iodide is, at ordinary temperatures, negative ( $-1600^\circ$ , Thomsen), but from the fact that the decomposition at temperatures such as 350—444° increases with rising temperatures, it follows from van't Hoff's principle (*Principe de l'équilibre mobile*) that the heat of formation at these

temperatures is positive. There must, therefore, be a temperature at which the heat of formation is zero, and at which also the decomposition is at a minimum. This point, as the experiments show, lies between  $310^{\circ}$  and  $350^{\circ}$ , and calculation by van't Hoff's formula showed that it is at  $324^{\circ}$ . As it was found that two bulbs heated under the same conditions always gave the same result, it was possible to study the decomposition as a time reaction, and by the formula given by Nernst. The constancy in the values actually obtained for each of the foregoing temperatures showed that, in the case of the decomposition of hydrogen iodide by heat, the change occurs in a perfectly regular manner (*Ber.*, 1893, 26, 1146; compare *Abstr.*, 1893, ii, 369).

This short account of Meyer's labours in physical chemistry may conclude with a brief reference to the determinations of the fusing points of salts melting only at relatively high temperatures, which he made in concert with his pupils. These he was able to obtain by the aid of the platinum air-thermometer he described in conjunction with Freyer. The following is a list of his final values :

Sodium chloride.....	815°	Sodium bichromate.....	878°
Sodium bromide.....	757	Sodium sulphate.....	863
Sodium iodide .....	661	Potassium sulphate	1078
Potassium chloride...	800	Cæsium iodide .....	621
Potassium bromide...	722	Calcium chloride ...	806
Potassium iodide ...	684	Strontium chloride...	832
Potassium carbonate	878	Barium chloride.....	921
Sodium carbonate ...	849	Rubidium iodide ...	641

(Compare Heycock and Neville, *Trans.*, 1895, 67, 190).

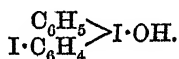
In 1892, Meyer and Wachter made known the possibility of the existence of a class of aromatic derivatives, known as the iodoso-compounds, in which the monovalent group IO replaces hydrogen. The first representative of the series was iodosobenzoic acid,  $C_7H_5IO_2$ , which they obtained by the action of fuming nitric acid or a boiling and acidified solution of potassium permanganate upon orthoiodobenzoic acid. It is a crystalline, solid substance, melting at about  $200^{\circ}$ , sparingly soluble in water or ether. It liberates iodine from potassium iodide, and chlorine from hydrochloric acid, forming orthoiodobenzoic acid. It is an extremely feeble acid, and its silver salt when dry is highly explosive.

No iodoso-derivatives could be obtained from meta- or para-iodobenzoic acids. Of the two iodoparatoluic acids, the one in which the iodine atom occupies the ortho-position to the carboxyl group yields an iodoso-derivative similar to iodosobenzoic acid, but the

isomeric acid does not yield a corresponding compound. If, however, *paraiodobenzoic acid* be previously nitrated, it may be converted by the further action of fuming nitric acid into an iodoso-derivative,  $\text{IO} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO}_2\text{H}$ . In like manner, the *iodoparatoluic acid* may be made to yield an iodoso-compound by previous nitration (*Ber.*, 1893, 26, 1354).

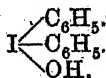
By the further action of oxygen on an alkaline solution of iodoso-benzoic acid, *iodoxybenzoic acid*,  $\text{IO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , is formed, a white, crystalline substance, turning red on exposure to light, and decomposing with explosion at  $233^\circ$ . It is a much stronger acid than the iodoso-derivative, forms moderately stable salts, and gives characteristic colour reactions with aniline and phenol (*Ber.*, 1893, 26, 1727; compare *Abstr.*, 1893, i, 577).

Hartmann and Meyer found that when *iodosobenzene*,  $\text{C}_6\text{H}_5 \cdot \text{IO}$ , is dissolved in strong sulphuric acid, the solution, on dilution with water, yields the sulphate of a base, *phenyliodophenyliodonium hydroxide*,

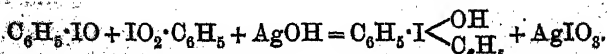


A similar change occurs with *paraiodosotoluene*. The free bases have a strong alkaline reaction, and form characteristic crystalline salts.

Meyer was thus led to the discovery of a remarkable group of substances known as the *iodonium compounds*, the simplest aromatic representative of which is *diphenyliodonium hydroxide*,

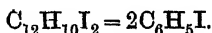


These bases are compounds in which two of the valencies of the iodine atom are satisfied by aromatic radicles whilst the third is satisfied in the free base by hydroxyl, and in the salts by an acid radicle. The iodonium bases are readily soluble in water, are strongly alkaline, and in their behaviour, as in that of their salts, show a remarkable similarity with the derivatives of silver, lead, and, more particularly, thallium. These bases are formed by the decomposition of the iodoso- and iodo-hydrocarbons under various conditions; for example, by the action of moist silver oxide upon an intimate mixture of equivalent proportions of *iodosobenzene* and *iodoxybenzene*,



By the addition of potassium iodide to the aqueous solution, *diphenyliodonium iodide* is precipitated. This compound stands in the same relation to *iodobenzene* that *trimethylsulphonium iodide* does to

methyl sulphide, and as tetramethylammonium iodide does to trimethylamine. It crystallises from alcohol in long, pale yellow needles, and decomposes on heating almost quantitatively into iodobenzene,



If the decomposition is started at one point, it proceeds through the whole mass with development of heat.

The existence of these remarkable bases and salts, which recall the sulphonium-, ammonium-, arsonium-compounds, &c., shows that a complex which is composed of one iodine atom and two molecules of phenyl, that is, of constituents which are otherwise negative, possesses strongly basic properties. From the general behaviour of the iodonium compounds, it is evident that the complex  $-\text{I} \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{smallmatrix}$  or

in general  $-\text{I} \begin{smallmatrix} \text{R} \\ \text{R}_1 \end{smallmatrix}$  (where R and R<sub>1</sub> are aromatic radicles) possesses the function of a metal analogous to thallium (compare *Lehrbuch der Organischen Chemie*, Meyer and Jacobson, 2, 127).

It is interesting to note that the physiological action of the diphenyliodonium chloride resembles that of ammonium salts on the one hand, and of heavy metals, such as lead and thallium, on the other. Doses of 0.02—0.03 gram produce total paralysis in frogs, both the motor nerve-ending and the muscle substance being affected. A dose of 0.08 per kilo. proves fatal to rabbits, the spinal chord and *medulla oblongata* being also affected.

A study of the conditions determining the formation and hydrolysis of ethereal salts of aromatic acids occupied Meyer, in conjunction with his pupils, and more especially Sudborough, from 1894 up to the year of his death. It was found that benzoic acid and its substituted products, as a rule, readily yield practically the theoretical quantity of an ethereal salt when treated with methyl alcohol and hydrochloric acid in the cold. On the other hand, the symmetrical trisubstitution products of benzoic acid yield no ethereal salts whatever under these conditions. This rule holds absolutely for all 1:3:5-trisubstitution derivatives of benzoic acid (Me, NO<sub>2</sub>, Cl, Br, I, and CO<sub>2</sub>H), except those containing one or more hydroxyl groups. The same is true of all substituted benzoic acids in which the 2:6-hydrogen atoms (CO<sub>2</sub>H = 1) have been replaced by other atoms or groups.

The acids which do not yield ethereal salts when treated with alcohol and hydrochloric acid can readily be converted into these substances by the action of methyl iodide on their silver salts, or of methyl alcohol on the acid chlorides.

This remarkable difference in behaviour may be ascribed to a stereochemical cause, the substituent groups being supposed to hinder the

introduction of the alkyl group to such an extent that under the prescribed conditions the reaction does not proceed.\* Acids in which the carboxyl group is linked with the benzene nucleus by one or more carbon atoms readily undergo etherification. The constitution of a substituted benzoic acid may, therefore, be ascertained in this way, and the method may also be used for isolating or purifying those acids which will not undergo etherification.

The nitrophthalic acids behave similarly: dinitrophthalic acid  $[\text{NO}_2:\text{CO}_2\text{H}:\text{CO}_2\text{H}:\text{NO}_2=1:2:3:4]$  gives no ethereal salt, whilst the acid  $[\text{NO}_2:\text{CO}_2\text{H}:\text{CO}_2\text{H}:\text{NO}_2=1:3:4:5]$  yields monalkyl salts. 1:2:6-Dinitrobenzoic acid gives no ethereal salt (Abstr., 1895, i, 93). Chloronitrobenzoic acid  $[\text{CO}_2\text{H}:\text{NO}_2:\text{Cl}=1:2:6]$  yields no ethereal salt, showing that the rule applies when the substituents are dissimilar. Diortho-substituted benzoic acids are not etherified at low temperatures when one of the substituents is hydroxyl.

Meyer was of opinion that etherification, in the case of analogous compounds, is diversely influenced by substituents of different relative mass. He imagined that those radicles which prevent etherification at high temperatures have a much greater relative mass than those which only hinder it at low temperatures, but it is probable that the methyl group and its normal homologues will produce almost identical effects, since the action is chiefly due to that carbon atom which is directly linked to the benzene nucleus. According to theory, those ethereal salts which are formed with greatest difficulty should be hydrolysed least readily, and such Meyer found to be generally the case.†

These conclusions have been tested by Kellas (*Zeit. phys. Chem.*, 1897, 24, 221), who has measured the velocity of etherification for a large number of monosubstitution derivatives of benzoic acid. From a study of the influence of temperature, and of the nature of the substituent, he has more precisely indicated the limits within which they may be regarded as generally true.

Considerations of space preclude more than a bare reference to the work on the derivatives of ethyl dinitrophenylacetate; on the indoxazen group; on the laws of substitution in the aliphatic series; on the synthesis of triphenylacrylonitrile and on the isomerides of triphenylacrylic acid; on the modes of introduction of acetyl groups into aromatic hydrocarbons; on the substitution of the hydrogen

\* This supposition has been modified by Wegscheider, who introduces Henry's conception of the formation of an additive compound between the alcohol and the acid. According to Wegscheider, the ortho-substituents prevent the formation of such additive compounds (compare, however, Davis, *Trans.*, 1900, 77, 33).

† This is approximately true for the benzoic series of acids, but does not obtain for the acetic and probably other series (compare Sudborough and Lloyd, *Trans.*, 1899, 75, 467).

in trinitrobenzene by alkaline metals; on the fusibility of platinum; on the formation of tetrindoethylene from diiodoacetylene; on the durenecarboxylic acids; on the action of potassium permanganate on hydrogen, methane, and carbon monoxide; on the slow oxidation of hydrogen and carbon; on the evolution of oxygen during reduction; on hexahydrobenzophenone and its oximes; and on diphenylamine from orthobromobenzoic acid.

Meyer contributed to the literature of chemistry, either alone or in conjunction with his pupils, upwards of 300 memoirs and papers.

No account of Meyer's scientific activity would be complete without some allusion to the various pieces of apparatus with which he enriched operative chemistry. Reference has already been made to his methods of determining vapour density, and to his mode of ascertaining the melting points of substances fusible only at high temperatures. He also greatly improved the methods of accurately determining the solubilities of substances at various temperatures. His form of water-bath is to be met with in many modern laboratories, surmounted, it may be, with the funnel-shaped cover which he devised to prevent access of dust to the evaporating liquid. Particularly neat and convenient are the drying ovens he constructed in which constant temperatures are obtained by means of liquids of different boiling points, for example, toluene, xylene, anisole, &c.

Analytical chemistry had little attraction for Meyer, and, beyond his mode of diagnosing primary, secondary, and tertiary alcohols and alcoholic radicles by colour reactions (see p. 180); and the method he devised, with Jannasch, for the simultaneous determination of carbon, hydrogen, and nitrogen in the elementary analysis of organic substances, he made no contribution to this department of the science.

As the director of a large chemical laboratory, and as a laboratory teacher, Meyer worthily followed in the footsteps of Bunsen. In proof of this, I may here quote the testimony of some of our Fellows who have worked under him.

Mr. John I. Watts thus refers to him in the Zürich days:

"Victor Meyer as a teacher had a wonderful faculty of infusing enthusiasm into his students. He was constantly in the laboratory, and whether the pupil was engaged upon the analysis of some simple, well-known substance, or was pursuing original investigation, he seemed somehow to succeed in making him feel how interesting was his work. Possessed of a very quick and active intelligence, he would point out the reason of the difficulties almost before the student had finished recounting them. He was himself a constant worker, and when engaged in his work he always appeared to be in a high state of pleasurable excitement."

Similar testimony is afforded by English chemists who were with him at Heidelberg. Dr. J. T. Hewitt writes:

"Professor Meyer was universally liked by the men who had the privilege of working under him. He had an extraordinary capacity for hard work, and his example, together with the interest he took in his men, induced in them a more or less similar love of work. After the morning lecture, which in the summer semester was at eight, he would come round the laboratory and see how every one was getting on, though of course he spent more time with those who were doing joint work with him than with those who were working with the other professors. We used very often to see him again during the morning, and at least once in the afternoon. In 1891, when I first went to Heidelberg, the most important work being done was on the slow combustion of electrolytic gas, and, not only those who were actually working on this subject, but every one else in the laboratory, used to take great interest in what was going on. Meyer's way of taking up old pieces of his work again and again meant that a very varied sort of work was done in the laboratory; for example, in consequence of Nef's criticism, nitro-fatty compounds were again examined, the result on the students being excellent, in that their general interest in chemistry was aroused. Meyer, as you well know, was an excellent speaker, not only in the lecture room, but in taking the chair at meetings of the Heidelberger Chemische Gesellschaft, when he was seen to great advantage."

Dr. Sudborough, who served him as an assistant when in Heidelberg, writes:

"As organiser and director of the laboratories, Meyer undoubtedly exhibited great business qualities, and everything worked extremely smoothly, owing probably to the fact that his staff had been with him for a number of years and were all on intimate terms of friendship with him. During the time I was an assistant, I had opportunities of observing with what care he entered into even the minutest financial details in connection with the department.

"In the laboratories he was extremely genial and pleasant, always having a kindly word for the students, and taking a great interest in their work. Characteristic, too, was the hopeful way in which he always looked forward to the successful termination of each piece of work, and by this means endeavoured to keep up the interest of the student. Every student who worked under him respected and honoured him as a scientific leader of the first rank, but in addition they felt a deep friendliness towards him on account of the kindly interest he took in them and in their work. A goodly percentage of those carrying out 'Arbeits' under him were either English or American; in fact, Meyer appears to have had a predilection for English and American students.

"Mention must also be made of Meyer's connection with the Heidelberg Chemical Society, of which he was an ardent supporter—in fact, may be said to have been its soul: he and Bernthsen (of the Badische Anilin- u. Soda-Fabrik) were the two presidents in my time and both were frequent contributors."

Dr. Jocelyn F. Thorpe writes:

"Perhaps that which impressed one most about Victor Meyer, besides his power and ability as an exponent and lecturer, was the faculty he possessed of conferring some of his enthusiasm upon the students who worked under him. Be his interest ever so slight and his knowledge of the subject ever so small,



no student could work long with Victor Meyer without feeling that he had a part in a system; that he was, in fact, one of the instruments by which the plans and ideas of a master mind were being shaped. Noticeable, too, was his wonderful power of grasping and remembering every little detail of the researches upon which he was at the moment engaged. At times, as many as thirty men would be working under him on subjects widely varying in character, yet in no case would he forget what each individual had been doing when he last visited him; occasionally he would astonish the student by asking him what had become of some (by the student) long-forgotten substance, the properties of which he could remember most distinctly.

"Every morning after his lecture he would enter the laboratories and personally not only visit the students who were working directly under him, but also those who were engaged in research with the other Professors and Privat-docenten of the department.

"Not only will Victor Meyer live in the memory of those who worked under him as a leader in chemistry, but many will remember him as the genial and kindly host. On many evenings during the semester he would give either supper parties or small dances, and occasionally a ball, to which his students were welcomed, and when his *camaraderie* and great tact were especially noticeable to those of us who, being foreigners newly arrived, were unacquainted with the language and social customs of his country.

"Towards the last his wonderful memory began to fail. I remember meeting him in Heidelberg the year before his death and asking him something, I cannot now remember what, but at any rate he was unable to answer me at the time, and asked me to call and see him the next day. He, however, stopped and tied a knot on his pocket handkerchief, saying, with a sad smile, 'my memory is not what it was.'"

Meyer's literary ability, combined with his power of lucid exposition, made him an admirable writer of what are called popular science articles. He was a frequent contributor to the *Naturwissenschaftlichen Rundschau*, and a number of his essays appeared under the title of "Aus Natur und Wissenschaft" (Heidelberg, 1892). His love of natural scenery and his power of graphically describing it may be seen in his "Märztage in Kanarischen Archipel" (Leipzig, 1893), a record of travel, written during the enforced rest following upon one of his too frequent periods of nervous prostration.

One who had studied him carefully and knew him well thus writes of his personal qualities and of the influence and attraction he exerted upon all who came in contact with him:

"Victor Meyer had a remarkable power over men. Where he entered, there he soon became the centre; each one listened to him, all collected round him. In the fascination he exercised there was nothing intentional or self-conscious; it was far less the influence of a commanding strength than the working of an incomparably attractive and many-sided nature. To this, too, his appearance contributed: the finely chiselled head with the splendid blue eyes might, at first sight, betoken the artist, were it not that there was in the expressive

features a rare blending of the lively temperament with the contemplative calm of the philosopher.

"In the circle of his fellows he captivated all by the eagerness with which he followed anything new, discussing and elucidating it in a manner peculiarly his own; by the joyous, often enthusiastic, recognition of other men's work, and by the warm-hearted interest he displayed in the scientific struggles of his juniors. In society, he showed himself an accomplished conversationalist and *raconteur*, an intelligent and warmly appreciative connoisseur of the arts of music and literature. As a host, he studied the comfort of every guest in his house. At the 'Biertisch' his sunny humour and overflowing wit diffused a general harmony; and his enthusiastic love of natural scenery made him the most delightful of travelling companions." (Paul Jacobson, in *Naturwiss. Rundschau*, 12, 43 and 44, p. 19).

Meyer's merits were recognised in every land where science is cultivated. He was a corresponding member of the Academies of Munich, Berlin, Upsala, and Göttingen, and an honorary member of many learned societies. The University of Königsberg made him an Honorary Doctor of Medicine. The Royal Society gave him the Davy Medal in 1891.

He was elected an Honorary Foreign Member of our Society in 1883, and attended the celebration of our Jubilee in the spring of 1891. Many of our Fellows will no doubt recall the stirring speech, instinct with a true eloquence, which he made at the banquet in responding to the toast of "Our Foreign Members," with its striking peroration:—"Möge die Chemical Society, neben allen ihren anderen schönen Aufgaben auch in Zukunft ihre völkerverbindenden Ziele in so erfolgreicher Weise anstreben wie bisher, möge Sie blühen und gedeihen als eine Pflegstätte der Wissenschaft, für ihr Vaterland vorerst, aber nicht minder für alle Völker welche sich im friedlichen Wettbewerb wissenschaftlicher Arbeit verbündet wissen."

May this aspiration be fulfilled! May the Chemical Society, in the years to come, continue, as in the past, to recognise, with a full and generous appreciation, the work of those across the seas who engage with us in the friendly rivalry of scientific labour!

And may our action in thus recording the services in our own annals of the gifted man whose

"prosperous labour fills  
The lips of men with honest praise,"

tend in some degree, however small, to that consummation for which he so earnestly and so eloquently pleaded!

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XVIII.—*Electrolytic Preparation of Induline Dyes.*

By EMERIQUE CHARLES SZARVASY, Ph.D.

It has long been known that different colouring matters are formed when the electric current is allowed to pass through solutions of aniline salts. The first experiments bearing on this subject were made by Letheby in 1862 (this Journ., 15, 161), who electrolysed a solution of aniline sulphate between platinum electrodes, the cathode being immersed in dilute sulphuric acid in a porous cell, and observed the formation of a bluish-green dye on the anode.

Goppelsröder (*Farbenalektrochemische Mittheilungen*, Mülhausen) electrolysed neutral or acid solutions of aniline salts; the dyes formed varied according to the salts, solvents, electrodes, and current densities employed. On electrolysing a solution of aniline hydrochloride for several hours, he obtained aniline-black mixed with small quantities of aniline-violet and "anilein." If the aniline contained toluidine, then mauvaniline, rosaniline, and leucaniline were also formed. Besides these colouring matters, he prepared a large number, the nature of which was not determined.

Voigt (*Zeit. angew. Chem.*, 1894, 107), on electrolysing concentrated solutions of aniline sulphate, obtained rosaniline, saffranine, chrys-aniline, and paraleucaniline.

Complex mixtures of colouring matters are evidently obtained by these methods, but no explanation has been given of the reactions which lead to their formation. In all probability, the production of dyes from aniline in this way is traceable primarily to the formation of azo-compounds by the action of electrolytic oxygen which may result either in the dehydrogenation of the amino-group and subsequent condensation, or in oxidation of the base to nitrobenzene and interaction of this with the excess of aniline. This view is supported by Rotondi's experiments (*Jahresber.*, 1884, 270), as azo-, diazo-, amidazo-, and diazo-amido-compounds were found among the products of the electrolysis of solutions of aniline.

These secondary effects necessarily complicate the reactions, but by far the greatest influence on the nature and quantity of the final products is exerted by the solvent, which, being ionisable, takes part in the electrolysis introducing new factors, which cause further secondary reactions.

On studying the electrolytic preparation of colouring matters, it occurred to me that the process could be essentially simplified by electrolysing the aniline salts in a fused state; the secondary reactions, due to the ionisation of the solvent, being eliminated, there

was good reason to hope for end products of a more homogeneous character.

The present paper gives an account of the principal results I have obtained by electrolysing fused mixtures of aniline and aniline hydrochloride, this salt being chosen as it has the advantage of melting comparatively easily and without decomposition.

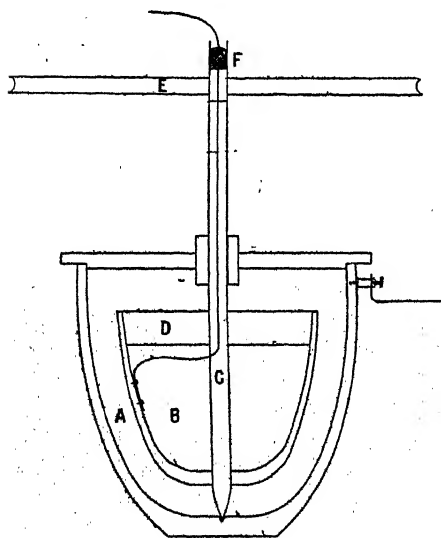
The preliminary experiments were made in glass tubes bent at right angles, the carbon electrodes being adjusted in the limbs of the tube, which was filled with aniline hydrochloride and kept at the desired temperature. When a current of 0.5—1 ampère was passed through the fused salt the mass soon turned blue. The colouring matter was formed on the anode, and could be better observed, when

loose asbestos, was packed in the bend of the tube forming a diaphragm. In this case, the dye was only formed in the limb containing the anode, that containing the cathode remaining colourless. When the direction of the current was reversed, the other side became coloured, and at the same time the blue colour on the cathode was slowly destroyed.

In the experiments on a larger scale, the substance was placed in a graphite crucible, *A*, which acted as the positive electrode. Another graphite crucible, *B*,

of suitable dimensions was connected with the negative pole by a copper wire, fastened to the inner wall of the crucible and passing through the glass tube, *C*, which served as a rotating axle. The upper part of *B* was closed with plaster of paris, *D*, to fix the axle and to protect the metallic connections. The contact between the two wire ends in *F* was effected by means of a mercury connection.

With the aid of a motor and the wheel, *E*, the inner crucible was slowly turned round and the melted mass kept in motion during the electrolysis, so that fresh portions of the mixture came into contact with the electrode. The large crucible was heated with a Bunsen burner, which was regulated to keep the fused mass at the desired temperature.



The active surface of the anode is about twice as large as that of the cathode, so that a higher current density on the cathode is attained and also the reducing action of the latter, which naturally tends to diminish the yield, is restrained.

The main advantage of this apparatus is that comparatively large quantities of the electrolyte form a thin layer between the two electrodes, and thus the resistance is very low. Graphite being a good conductor of heat, the temperature of the fused mass is uniform, this being an important condition in these reactions.

I may mention that this apparatus is very suitable for electrolysing substances of high melting points, the only alteration to be made in this case being that the glass tube forming the axle is replaced by one of porcelain.

After the electrolysis was completed, the product was poured into a flask, diluted with water, the excess of aniline hydrochloride decomposed with sodium carbonate and the aniline removed by distillation with steam. The coloured substance remaining in the distillation flask was purified by subsequent washing with water and ether, and then extracted with methyl alcohol, in which it was very soluble. After extraction, a black powder remained, which consisted chiefly of aniline black, mixed with small quantities of graphite from the electrodes. The quantity of aniline black varied according to the conditions under which the electrolysis was carried out, as high current density and high temperature tend to increase the amount, whereas, under other conditions, very little is formed.

This method, which merely separates the indulines from aniline black, was employed in determining the quantities of the products formed and ascertaining the most favourable conditions under which the current efficiency is the highest. The results obtained are arranged in the table on p. 210. In columns  $D_a$  and  $D_c$  respectively, the current densities on the anode and cathode are given, the numbers being calculated in amperes per square decimetre of electrode surface.

Experiments 1—7 were made to determine the influence of current density, 8—11 that of the duration of the action, and 12—15 that of temperature. It will be seen that when  $D_a$  is approximately 0.8, the efficiency of the current is at its highest, but at the same time the temperature must be maintained at about 160°. The experiments also show that as the electrolytic action is prolonged, the product per unit of electric energy becomes less, so that only 20 per cent. of the original material can be profitably transformed into the dye, but as the aniline is recovered almost quantitatively, when separating the products, the yield amounts to 86—90 per cent. of that actually used.

The colouring matter extracted with methyl alcohol consists of a

Series.	Volt.	$D_a$ .	$D_c$ .	Duration of experiments in hours.	Temperature.	Product in grams per 1 amp. hour.
1	2.9—3.2	0.57	1.2	3	160°	1.64
2	3 — 3.2	0.7	1.48	3	160	2.0
3	3 — 3.5	0.8	1.7	3	160	2.5
4	3.2—5	1.03	2.2	3	160	2.1
5	4.5—5	1.12	2.5	3	160	1.86
6	5.4—7	2.2	4.5	3	160	1.54
7	10 —12	3.2	5.5	3	160	1.45
8	3 — 3.5	0.8	1.7	2	160	2.7
9	3 — 3.5	0.8	1.7	5	160	1.9
10	3 — 3.5	0.8	1.7	8	160	1.3
11	3 — 3.5	0.8	1.7	16	160	0.61
12	5 — 7	0.8	1.7	3	120	1.8
13	4 — 5	0.8	1.7	3	150	2.3
14	2 — 3	0.8	1.7	3	180	1.67
15	2 — 3	0.8	1.7	3	210	1.1

mixture of hydrochlorides of bases of the induline class, and in acid solution dyes silk or wool, but has no affinity for cotton. It may be remarked that this mode of preparation resembles the well known "induline process," inasmuch as a mixture of indulines is produced, the nature of which, as well as the proportions existing between the constituents obtained, depends largely upon the temperature at which the reaction takes place and the manner in which it is conducted.

#### *Separation of the Dyes.*

When electrolysing with low current density at a comparatively low temperature, several colouring matters are formed, which are soluble in water; from these I succeeded in separating "induline" and " $B_{2,4}$  anilinoinduline," first described by O. Fischer and Hepp (*Annalen*, 256, 262, 266, 272, 286).

The colouring matter was dissolved in 50 per cent. acetic acid, and concentrated hydrochloric acid was added to the violet solution. After some time, a crystalline precipitate, *A*, separated, which was removed by filtration. Sodium chloride was then added to the filtrate, and a precipitate, *B*, obtained consisting of a mixture of several dyes which dissolved in hot water forming a dark blue solution.

*Precipitate B.*—The aqueous solution, on the addition of caustic soda, gave a precipitate which was soluble in benzene, and from the solution after concentration small crystals were obtained. After recrystallising several times from a mixture of light petroleum and benzene, the product was obtained in reddish-brown needles; it

melted at about  $206^{\circ}$ , and dissolved in concentrated sulphuric acid with a violet colour. On analysis, it proved to be induline.

Found C=79.37; H=4.9; N=15.35 per cent.

$C_{18}H_{13}N_3$  requires C=79.70; H=4.79; N=15.49 per cent.

*Precipitate A.*—This precipitate was examined in the same way, the crystalline powder which separated from the solution in benzene being recrystallised several times from this solvent. When pure, the product formed small prisms with a metallic lustre, and melted at about  $150^{\circ}$ . It dissolved in strong sulphuric acid with a dark blue colour, which, on the addition of water, became violet. On analysis it gave numbers agreeing with those required for "B<sub>2</sub>,4 anilino-induline."

Found C=79.73; H=5.30; N=15.22 per cent.

$C_{24}H_{18}N_4$  requires C=79.55; H=4.98; N=15.47 per cent.

When the conditions of experiment were varied by increasing the current density, and the temperature was maintained at  $160$ — $170^{\circ}$  during the electrolysis, it was found that only small quantities of soluble indulines were formed, and that the "induline 6B," described by Witt and Thomas (Trans., 1883, 43, 112), occurred among the products. This separated in a crystalline form when the fused mass was allowed to cool very slowly, and was freed from soluble indulines by filtration and subsequent washing with alcohol, in which it is almost insoluble. It was then treated with alcoholic caustic soda, and the resulting base, after washing with water and then with dilute alcohol, was purified by repeated recrystallisation from aniline, from which it separated in greenish, glistening crystals. On analysis, it gave numbers agreeing with those required for "induline 6B."

Found C=81.78; H=5.23; N=13.10 per cent.

$C_{36}H_{27}N_5$  requires C=81.66; H=5.11; N=13.23 per cent.

#### *Theory of the Process—Electrolytic Preparation of Azophenine.*

Induline dyes are formed by the action of azo- and amidoazo-compounds on the hydrochlorides of aromatic amines; as an intermediate product, azophenine is formed, which plays a most important part in the formation of indulines. The formation of this compound is in all probability due to the oxidising effects of the azo-compounds, which decompose into *p*-phenylenediamine and aniline with the elimination of ammonia. With these bases, the azophenine reacts yielding indulines.

Only small quantities of the azo-compounds are found in the products of electrolysis, as immediately after their formation interaction with the aniline hydrochloride takes place. However, it is certain

that azo-compounds are the primary products, and are present in the early stages of the reaction. Their formation may be explained as follows. By the electrolytic decomposition of the aniline hydrochloride, chlorine is liberated at the anode, and reacting with the aminic hydrogen of the aniline effects dehydrogenation with the production of hydrogen chloride, hydrazobenzene, and azobenzene. So far as I am aware, only one instance of a similar reaction has yet been recorded, namely, the formation of azobenzene by the action of bleaching powder on aniline dissolved in chloroform (Schmitt, *J. pr. Chem.*, 1878, [ii], 18, 196). As a rule, the halogens, when reacting with aniline, give rise to the formation of substitution products.

Azophenine can be detected in the product of the electrolysis of a mixture of aniline hydrochloride and aniline, and may be obtained in considerable amount if the temperature is kept at 70—90° during the reaction.

In one experiment, after the electrolysis had continued for 2—3 hours, the product, after treatment with sodium carbonate and removal of the excess of aniline, formed a brownish powder, which, after being washed with hot water and alcohol, was dissolved in aniline. From this solution, brownish-red crystals separated, which, after re-crystallisation from benzene, melted at 239°. On analysis, it gave numbers agreeing with those calculated for azophenine.

Found C = 82.05; H = 5.67; N = 12.73 per cent.

$C_{10}H_9N_3$  requires C = 81.36; H = 5.46; N = 13.18 per cent.

The substance formed a violet solution in concentrated sulphuric acid, gave a violet mass when heated with *p*-phenylenediamine hydrochloride, and, on reduction with tin and hydrochloric acid, formed a mixture of bases, among which aniline and *p*-phenylenediamine were detected.

Briefly summarised, the results prove that (1) the chlorine produced by the electrolytic decomposition of aniline hydrochloride effects dehydrogenation of aniline; (2) under certain conditions, the azo-compounds thus formed interact with the aniline hydrochloride, forming (3) primarily azophenine, and (4) ultimately indulines.

I propose to extend these investigations to the homologues of aniline and some other aromatic amines, and the results will, in due course, be communicated to the Society.

This research has been carried on in the Davy-Faraday Research Laboratory of the Royal Institution, and I take this opportunity of tendering my thanks to the Directors and to Dr. A. Scott for the facilities they have given me.

DAVY-FARADAY RESEARCH LABORATORY,  
ROYAL INSTITUTION,



# XIX.—Action of Chloroform and Potassium Hydroxide on o-Aminobenzoic Acid.

By WALTER J. ELLIOTT, M.A.

In a previous communication (Trans., 1896, 69, 1513), it has been shown that when chloroform and potassium hydroxide act on *m*-aminobenzoic acid under certain conditions, a compound is produced which condenses with phenylhydrazine, but does not yield a hydrazone. The results of analysis pointed to the formation of a compound of the formula  $\text{NH}_2 \cdot \text{C}_6\text{H}_5(\text{CO}_2\text{H}) \cdot \text{CHO}$ .

The study of the action taking place when o-aminobenzoic acid is substituted for the meta-derivative has afforded further evidence of the formation of aldehydes, a hydrazone and semicarbazone having been isolated. Unfortunately, the yield is so small and the substance so soluble that the pure aldehyde has not been obtained, but derivatives have been prepared and analysed. Numerous attempts have been made to increase the yield with but slight success. The product, however, is more stable than that obtained from the meta-acid.

It has been shown (Trans., 1898, 73, 145) that o-nitrobenzoic acid is far more stable towards chloroform and potassium hydroxide than the meta- and para-acids; the o-amino-acid has also proved to be more stable towards these agents than its isomerides.

The compound obtained from the meta-acid readily decomposes when boiled with water, yielding *m*-aminobenzoic acid again, and it was suggested (Trans., 1896, 69, 1517) that the decomposition was preceded by oxidation to aminophthalic acid, which, according to Miller (*Annalen*, 1881, 208, 245), decomposes with the formation of *m*-aminobenzoic acid. The greater stability of the compound formed from the ortho-acid can be understood if the aldehyde group does not enter the molecule in the ortho-position relatively to the carboxyl group as it does probably in the product from the meta-acid. Experiments have been carried out with *p*-aminobenzoic acid which promise interesting results bearing on this point, and I hope shortly to resume the work.

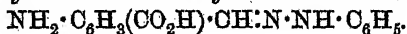
## EXPERIMENTAL.

The method adopted in the case of *m*-aminobenzoic acid (*loc. cit.*) was tried. 10 grams of o-aminobenzoic acid were added to a solution of 20 grams of potassium hydroxide in about 200 c.c. of water, and the solution was boiled with 14 grams of chloroform for 45 minutes.

After acidifying with acetic acid, no precipitate was at first obtained, but on standing, crystals separated, which proved to be unchanged *o*-aminobenzoic acid (m. p. 144°). Numerous similar experiments were made with varied proportions of the reacting substances and of water, but with similar results. When concentrated solutions were boiled for a long time, a small quantity of a reddish, resinous substance was precipitated by acetic acid; the amount, however, was too small to admit of further examination.

As no insoluble product had been obtained, dilute sulphuric acid was substituted for acetic acid, and the product, after acidification, was shaken with ether. The residue, after distilling off the ether, was crystallised from water; *o*-aminobenzoic acid separated out at first, but on concentrating the mother liquor, crystals were obtained having a melting point considerably below that of this substance. A solution of phenylhydrazine in acetic acid gave, with the mother liquor, a yellow precipitate at once. All attempts to isolate the aldehydo-acid from the ether extract have failed, as no medium has been found to separate it from *o*-aminobenzoic acid. The phenylhydrazone, however, has been prepared in sufficient quantity for examination and analysis, although the task has been laborious, the yield being very small.

*Phenylhydrazone of Aldehydo-o-aminobenzoic Acid,*



The method finally adopted for the preparation of the phenylhydrazone was as follows: 10 grams of *o*-aminobenzoic acid were dissolved in a solution of 30 grams of potassium hydroxide in 150 c.c. of water, and the solution heated to a temperature of 60° in a flask fitted with a reflux condenser; 16 grams of chloroform were added gradually, and the mixture heated for 3 hours. When cold, the product was acidified with excess of acetic acid, allowed to stand for an hour, filtered from crystals of the original acid, and treated with a solution of phenylhydrazine in acetic acid. The phenylhydrazone separated on standing as a bulky, yellow precipitate. It was washed with hot water, and crystallised twice from alcohol. The filtrate from the phenylhydrazone, when evaporated to a small bulk, treated with dilute sulphuric acid, and shaken with ether, yielded a large quantity of the original *o*-amino-acid.

The recrystallised phenylhydrazone separated in small, yellow needles which melted at 230°. It was insoluble in water, but fairly easily soluble in alcohol. The yield of the pure substance obtained from 10 grams of the acid never exceeded 0.5 gram.

On analysis, the following numbers were obtained :

0.1445 gave 0.3476  $\text{CO}_2$  and 0.0700  $\text{H}_2\text{O}$ .  $\text{C} = 65.60$ ;  $\text{H} = 5.09$ .  
 0.1997 „ 0.4827  $\text{CO}_2$  „ 0.0946  $\text{H}_2\text{O}$ .  $\text{C} = 65.91$ ;  $\text{H} = 5.25$ .  
 0.1092 „ 14.9 c.c. moist nitrogen at  $13^\circ$  and 763 mm.  $\text{N} = 16.04$ .  
 0.1134 „ 16.2 c.c. „ „  $15^\circ$  „ 752 mm.  $\text{N} = 16.37$ .  
 $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3$  requires  $\text{C} = 65.88$ ;  $\text{H} = 5.09$ ;  $\text{N} = 16.47$  per cent.

Numerous attempts have been made to obtain the aldehydo-acid from the hydrazone but without success. When boiled with dilute hydrochloric or sulphuric acid, the hydrazone dissolved, but was reprecipitated unchanged on carefully neutralising the solution. Decomposition apparently occurred with concentrated hydrochloric acid, but no definite product could be isolated, possibly owing to the small quantity of hydrazone available.

One remarkable property of this substance is its power of forming salts sufficiently stable for analysis. The barium and silver salts have been prepared and analysed.

*Barium Salt.*—A dilute solution of ammonia was neutralised by excess of the hydrazone, filtered and treated with barium chloride solution. A yellow, crystalline precipitate separated, which was washed well with water and dried in a vacuum. It was found impossible to recrystallise the salt, as decomposition occurred on heating with water.

0.2574 gave 0.0957  $\text{BaSO}_4$ .  $\text{Ba} = 21.86$ .  
 $(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_3)_2\text{Ba}$  requires  $\text{Ba} = 21.24$  per cent.

*Silver Salt.*—This salt is unstable but can be isolated if care is taken to exclude light during the preparation and to use cold solutions only. The hydrazone was dissolved in dilute ammonia solution, very dilute nitric acid was added until a precipitate just appeared, the solution was then filtered and silver nitrate solution added. The light yellow precipitate obtained was washed well with cold water and dried in a vacuum.

0.1244 gave 0.0378  $\text{Ag}$ .  $\text{Ag} = 30.38$ .  
 $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_3\text{Ag}$  requires  $\text{Ag} = 29.83$  per cent.

#### *Semicarbazone of Aldehydo-o-aminobenzoic Acid.*

When a solution of semicarbazide hydrochloride was added to the filtrate obtained after acidifying the condensation product, as already described, a yellow precipitate separated on standing, which proved on analysis to be the semicarbazone of an aldehydo-o-aminobenzoic acid. The yield is even smaller than that of the phenylhydrazone.

The semicarbazone is insoluble in water, and only sparingly soluble in alcohol, from which it separates in greenish-yellow, microscopic crystals melting at  $246^\circ$ .

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0.1462 gave 33.5 c.c. moist nitrogen at  $22^\circ$  and 757 mm.  $N = 25.39$ .

$C_9H_{10}O_3N_4$  requires  $N = 25.22$  per cent.

All attempts to prepare the aldehydo-acid from the semicarbazone have failed.

I hope to be able to publish in due course the results of an investigation of the action of chloroform and potassium hydroxide on *p*-aminobenzoic acid.

## XX.—*Anhydrous Sulphates of the Form $2M''SO_4.R'_2SO_4$ ; especially those of Isometric Crystallisation.*

By FREDERIC R. MALLET.

THE mineral known as langbeinite was so named by Zuckschwerdt, who published a description of specimens from near Halberstadt, in Prussian Saxony, in 1891 (*Zeit. angew. Chem.*, 1891, 356), his analyses of the substance being in close agreement with the formula  $2MgSO_4.K_2SO_4$ . Crystals of the mineral were first discovered in 1897, by Siebert, and examined by Luedecke, who showed that they belonged to the tetartohedral group of the isometric system (*Zeit. Kryst. Min.*, 1898, 29, 255). So far as I have been able to ascertain, the mineral constitutes the first known example, either natural or artificial, of an anhydrous sulphate with the composition expressed by  $2M''SO_4.R'_2SO_4$ , and, after some investigation into the literature of the subject, I have met with descriptions of only two other analogous salts; namely,  $2CuSO_4.(NH_4)_2SO_4$ , produced by Klobb in 1892 (*Compt. rend.*, 1892, 115, 230), and  $2MnSO_4.(NH_4)_2SO_4$ , formed by Lepierre in 1895 (*Compt. rend.*, 1895, 120, 924). The copper salt was prepared by melting one part of crystallised cupric sulphate with three parts of ammonium sulphate, and driving off the excess of the latter by gentle heat, the double salt remaining in "prisms." In obtaining the manganese compound, one part of crystallised manganese sulphate was fused with five parts of ammonium hydrogen sulphate, the excess of the latter decanted off, and the double salt, which forms isometric crystals, purified with boiling alcohol. Nickel and cobalt sulphates, treated like manganese sulphate, yielded salts of the composition  $3M''SO_4.2(NH_4)_2SO_4$  (*Compt. rend.*, 1892, 115, 115).

During an examination of langbeinite, from the Mayo salt mines in the Punjab, a short account of which was read before the Mineralogical Society last April (*Min. Mag.*, 1899, 12, 159), I noticed that

the mineral, which fuses at a red heat, on cooling solidifies to a more or less distinctly crystallised mass. This observation naturally suggested that the salt might probably be artificially produced by the simple expedient of fusing magnesium sulphate and potassium sulphate together in the proper molecular proportion. On putting the question to the test, excellent results were obtained, the fused mixture solidifying to a highly crystalline mass, including, under favourable conditions, a large drusy cavity in the interior, lined by numerous well-formed octahedral crystals, often more than a millimetre in diameter.

As it seemed probable that other salts of similar constitution might be formed in the same way, I have spent some time lately in attempting their production, and a considerable number have been prepared; some of isometric crystallisation, like langbeinite, others in crystals with symmetry of lower grade.

The sulphates of the bivalent and of the univalent metals fuse together at temperatures which vary considerably in different cases. Thus, the mixed salts of zinc and potassium melt below redness; those of magnesium and potassium require a full red heat; a yellow heat is necessary with the sulphates of calcium and potassium, whilst for those of barium and potassium an incipient white heat is requisite. In all cases, the colourless mixtures fuse to a clear, transparent liquid. At the temperature of fusion, or not much above it, the mixed sulphates are in some cases nearly stable, scarcely any bubbles being given off, but, more commonly, such are eliminated, comparatively slowly in some instances, quite freely in others, a certain amount of sulphur trioxide being expelled, and a corresponding quantity of oxide of the bivalent metal disseminated through the product. If the temperature, however, is not raised unnecessarily high, and the material is allowed to cool as soon as fusion is complete, it dissolves in most cases so nearly perfectly in water that only a trifling residue—sometimes not more than an unweighable trace—of oxide is found in suspension.

The mixtures were generally dehydrated before fusion, in order to avoid the inconvenient intumescence which otherwise occurs. Except in the case of salts liable to partial reduction on heating, the fusions were made in a platinum crucible. If allowed to cool therein, the product can sometimes be shaken out, but, as a rule, the fused material was poured into a (subsequently covered) nickel crucible, to which it very rarely adheres when cold. Different salts require somewhat different treatment in obtaining the best results as to crystallisation. Thus, finer crystals of  $2\text{MgSO}_4, \text{K}_2\text{SO}_4$  were obtained by heating the mould nearly to redness, before pouring in the fused mass, than when the latter was cooled either more quickly or more

slowly. The corresponding rubidium salt, on the other hand, crystallised better when poured into a cool mould. As a general rule, the most favourable results were obtained when the salts were cast at the lowest possible temperature. There is generally a certain amount of crepitation during the cooling and crystallisation of the material, which is more marked in some cases than in others.

The first question which suggests itself in respect to the products, is whether they are homogeneous, in other words, whether they are composed of one salt, or more than one; and, in this connection, whether the crystals lining the drusy cavities have the same composition as the rest of the material. In so far as the products displaying isometric characters are concerned, there is conclusive evidence that but one salt is present in each.

(1) The crystallisation is the same throughout, although the crystals in the cavities, which are frequently attached on one side only, are naturally the most perfectly developed, the whole of the upper (free) surface of the mass is generally covered by crystalline facets of the same kind, and the fractured surfaces of the material throughout display crystals, or at least crystal faces, similar to those in the cavities.

(2) When fragments,\* whether from the cavities or elsewhere, are examined under the microscope in parallel polarised light, all are isotropic.†

(3) Fragments of the highly-coloured products containing nickel or cobalt, when examined with the microscope, show no indication, by difference in colour, of two salts being present.

(4) In view of the above, it would be unnecessary labour to analyse the crystals in the cavities and the general mass of the substance separately, in the case of each salt. This has, however, been done in respect to the magnesium potassium sulphate, which may be regarded as the type of the series, and it has been found, as shown by the analyses given below, that the least crystalline part of the fusion, that nearest to the mould, which cooled most rapidly, and the crystals in the cavities, have the same composition.

\* Preferably mounted in Canada balsam.

† Sometimes a few scattered birefringent specks, forming a quite insignificant portion of the whole material, are included in the isotropic fragments; in other cases none are visible. Where present, they are probably due to the original mixture of sulphates not having been in perfect molecular proportion, or to the proportion being slightly altered, during fusion, by the elimination of sulphur trioxide, previously alluded to, whereby a minute excess of  $R'_2SO_4$  is induced.

## I. ISOMETRIC SALTS.

*Magnesium Potassium Sulphate*,  $2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$ .

The mixed salts fuse at a full red heat, and during the cooling of the mass there is usually considerable intumescence, some of the material from the still liquid interior erupting through the surface crust. On breaking the solidified mass, a drusy cavity is found in the interior, which is of large size when the conditions of cooling have been most favourable. The walls of the cavity are thickly covered by crystals, which are, geometrically, octahedrons, the eight faces being approximately equally developed. The faces are most commonly smooth and lustrous, but are often more or less cavernous, the edges of the hollows being parallel to those of the crystal faces. In many cases, the octahedral edges are replaced by faces of the rhombic dodecahedron. The crystals show a very strong tendency to group themselves with parallel orientation, as one result of which columns composed of interpenetrant octahedrons, with their vertical axes in line, are of frequent occurrence. Measurements of the crystal angles with a reflecting goniometer are given below.

	Measured.	Calculated.
111 $\wedge$ 111.....	70° 33'	70° 32'
111 $\wedge$ 110.....	35 16	35 16

In accordance with Luedecke's determination of the natural crystals from Bernburg (*loc. cit.*) as belonging to the tetartohedral group, it would seem that the octahedral faces on the artificial ones should be regarded as those of two tetrahedrons of opposite sign, and in this connection it is noteworthy that a tetrahedron is the predominant, or only, form in the corresponding salts of zinc, manganese, and cobalt. Attempts to settle the point by etching the crystals were not very decisive. When exposed to water, or damp air, for some time, the faces of one set seem to become dull more quickly than those of the other, but the difference is not very sharply marked. The loss of lustre is due to the surfaces becoming pitted by numerous triangular hollows of the same character as the larger ones which produce the cavernous crystals.

The crystals obtained by fusion, on which only the forms mentioned above have been noticed, are simpler than the natural ones examined by Luedecke, which were presumably formed from solution, and on which he discovered eight or nine different kinds of faces.

Employing material from the same fusion, well-developed crystals from the interior, and a portion from the least crystalline part (nearest the mould), were analysed separately, with the following results :

	Crystals	Exterior.	Calculated.
SO <sub>3</sub> .....	57·83	57·92	57·89
MgO.....	19·29	19·28	19·41
K <sub>2</sub> O .....	[22·88]	[22·80]	22·70
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

A portion of the salt, exposed in powder to the air until it ceased to gain in weight, was found to have increased 56·26 per cent.,\* an increase of 56·44 per cent. being equivalent to 13H<sub>2</sub>O. Decomposition by hydration, therefore, evidently takes place in accordance with the equation :



or, in the case of the natural alteration of the mineral, one molecule of langbeinite is converted into one molecule of picromerite, and one of epsomite (*Min. Mag.*, 1899, 12, 163).

#### *Zinc Potassium Sulphate, 2ZnSO<sub>4</sub>.K<sub>2</sub>SO<sub>4</sub>.*

This salt fuses below a red heat, or at a lower temperature than any of the other potassium double salts examined. None of them (2ZnSO<sub>4</sub>.K<sub>2</sub>SO<sub>4</sub> included) intumescs on cooling as much as the magnesium salt just described; the masses obtained do not include equally large cavities, and although well-developed crystals are to be found in the latter, they do not occur in such profusion.

The salt crystallises in unmodified tetrahedrons, the faces of which are generally striated parallel to the edges. The crystals are frequently more or less cavernous. Owing to the concavity of the faces, the angles are ill-adapted for measurement by the reflecting goniometer, but measurement by contact showed no indication of divergence from the calculated (actual) angle of 70°32'.

On analysis :

SO<sub>3</sub> found = 48·29 ; calculated = 48·31 per cent.

When the salt was exposed to the air until the weight no longer increased, the absorption amounted to 46·74 per cent., 13H<sub>2</sub>O requiring 47·10; the salt therefore decomposes in the same way as the previous one.

\* In weather of rather less than medium humidity. The absorption varies, to some extent, with the humidity of the air, and the products of hydration cannot be dried by H<sub>2</sub>SO<sub>4</sub>, as efflorescence then takes place. The same remark applies to the salts described in the sequel.



*Manganese Potassium Sulphate*,  $2\text{MnSO}_4, \text{K}_2\text{SO}_4$ .

The salt forms pale reddish, unmodified tetrahedrons, with faces which are generally smooth and lustrous, but sometimes cavernous.

	Measured.	Calculated.
111 $\wedge$ $\bar{1}\bar{1}\bar{1}$ .....	109°28'.	109°28'.

The crystals show a tendency to group themselves with parallel orientation, and sometimes form columns composed of interpenetrant tetrahedrons in parallel position.

On analysis :

$\text{SO}_3$  found = 50·46 ; calculated = 50·42 per cent.

After exposure to the air until no further increase of weight took place, the absorption amounted to between 0·26 and 0·86 per cent. (according to the weather), which was evidently due to hygroscopic moisture only. In its stability, under the circumstances, the manganese potassium salt differs from the corresponding sulphates of magnesium, zinc, nickel, and cobalt ; and its non-decomposition by hydration, in accordance with an equation similar to that given for  $2\text{MgSO}_4, \text{K}_2\text{SO}_4$ , is in agreement with the experience of Tutton and others, who have been unsuccessful in all attempts to produce the salt  $\text{MnSO}_4, \text{K}_2\text{SO}_4, 6\text{H}_2\text{O}$  (Trans., 1893, 63, 342 ; 1896, 69, 399).

*Nickel Potassium Sulphate*,  $2\text{NiSO}_4, \text{K}_2\text{SO}_4$ .

The brownish-yellow crystals of this salt are, geometrically, octahedrons, but sometimes there is a certain amount of inequality in size between the two sets of planes, suggestive of + and - tetrahedrons. The solid angles of the octahedrons are occasionally truncated by minute faces of the cube.

	Measured.	Calculated.
111 $\wedge$ $\bar{1}\bar{1}\bar{1}$ =	70°33'	70°32'
111 $\wedge$ 100 =	54 47	54 44

The crystals tend to group themselves with parallel orientation.

A slight, but quite weighable, residue of nickel oxide was left on dissolving the salt in water, indicating loss of sulphur trioxide during fusion.

On analysis :

$\text{SO}_3$  found = 49·52 ; calculated = 49·65 per cent.

On exposure to the atmosphere, the salt absorbs a large amount of water, but the exact proportion is difficult to estimate, on account of

efflorescence in air of medium humidity, and deliquescence when the air is damp. Results varying from  $43\frac{1}{2}$  to 53 per cent., and more, were obtained,  $13H_2O$  requiring 48.41.

*Cobalt Potassium Sulphate*,  $2CoSO_4.K_2SO_4$ .

The salt is violet when hot and purplish-crimson after cooling, the crystals, as a rule, being somewhat more complex than those previously described. The predominant form is a tetrahedron, of which the trihedral solid angles are truncated by the faces of the tetrahedron of opposite sign, whilst the edges are frequently truncated by faces of the cube. The edges, again, between the + and - tetrahedrons are sometimes replaced by very minute planes, which are, apparently, those of the rhombic dodecahedron, as they seem to make equal angles with the tetrahedral faces. Some crystals, also, are met with showing the faces of an unmodified tetrahedron only. Not unfrequently, the crystals are distorted by elongation parallel to one edge of the predominant tetrahedron.

	Measured.	Calculated.
111 $\wedge$ 1 $\bar{1}\bar{1}$ .....	108°53'	109°28'
111 $\wedge$ 1 $\bar{1}1$ .....	70 14	70 32
111 $\wedge$ 100.....	54 27	54 44

The crystals are minute, but excellently developed, with smooth faces which have a considerable lustre when the mass of salt is first broken up. As this brilliancy is quickly lost on exposure to the air, the crystals measured were dipped in a dilute solution of Canada balsam in benzene, but even so the reflections were unsatisfactory. Hence, doubtless, the discrepancy between the measured and calculated angles. The crystals show a strong tendency to arrange themselves with parallel orientation.

A slight, but quite weighable, residue of cobalt oxide was left on dissolving the salt in water, indicating loss of sulphur trioxide during fusion.

On analysis:

$SO_3$  found = 49.34; calculated = 49.59 per cent.

On exposing the salt to the air until no further gain in weight took place, the increase amounted to 46.53 per cent., equivalent to about  $12\frac{1}{2}H_2O$ ,  $13H_2O$  requiring 48.35 per cent. The deficiency is probably due to the tendency of  $CoSO_4.7H_2O$  to effloresce.

*Ferrous Potassium Sulphate*,  $2FeSO_4.K_2SO_4$  (?).

As ferrous iron is associated with the preceding five bivalent metals in more than one series of isomorphous salts, it would, perhaps,

not be surprising if the compound  $2\text{FeSO}_4 \cdot \text{K}_2\text{SO}_4$  were found to crystallise in the isometric system. Whatever the possibilities of producing the salt in the wet way may be, it does not seem feasible to prepare it by fusion on account of the facility with which the ferrous sulphate decomposes and ferric oxide is produced. As the oxidation may take place by means of oxygen present in the sulphate, it cannot be prevented by effecting the fusion in a current of hydrogen.

*Magnesium Rubidium Sulphate,  $2\text{MgSO}_4 \cdot \text{Rb}_2\text{SO}_4$ .*

Magnesium rubidium sulphate crystallises almost as freely as the corresponding salt of potassium. The crystals are, geometrically, octahedral, with the edges often replaced by narrow faces of the rhombic dodecahedron.

	Measured.	Calculated.
$111 \wedge \bar{1}\bar{1}\bar{1} =$	$70^\circ 29'$	$70^\circ 32'$
$111 \wedge 110 =$	$35 \ 15$	$35 \ 16$

The crystals display a strong tendency to group themselves with parallel orientation. As one result of this, crystals resembling tetragonal prisms, with pyramidal terminations, are very common; they are made up of numerous interpenetrant octahedrons, having their vertical axes in line, and their centres so close together that, on each side of the pseudo-prism, the lateral dodecahedral faces are united into one plane without striations. Very frequently one pair of octahedral faces, for example,  $111$  and  $\bar{1}\bar{1}\bar{1}$ , are comparatively large and cavernous, whilst the adjoining pair,  $1\bar{1}1$  and  $\bar{1}1\bar{1}$ , are rather smaller and smooth, and, where many crystals are in parallel position, those faces which are similarly oriented are respectively cavernous or smooth. It is difficult to isolate crystals showing all eight octahedral faces so as to determine more decisively whether those of the positive and negative octants are differentiated in the way just indicated.

On analysis :

$\text{SO}_3$  found =  $47.42$  ; calculated =  $47.32$  per cent.

On exposure to the air until the weight no longer increased, the salt absorbed  $45.71$  per cent. of water,  $13\text{H}_2\text{O}$  requiring  $46.14$ .

*Mixed Crystals.*

The preceding include all the isometric double salts which have been prepared (rubidium and caesium sulphates yielding, with the one exception just described, birefringent crystals when fused with those of the preceding bivalent metals). Some mixed crystals, however, such as  $\text{MgSO}_4 \cdot \text{MnSO}_4 \cdot \text{K}_2\text{SO}_4$  ;  $\text{MgSO}_4 \cdot \text{NiSO}_4 \cdot \text{K}_2\text{SO}_4$  ;

$\text{MgSO}_4$ ,  $\text{CoSO}_4$ ,  $\text{K}_2\text{SO}_4$ ;  $\text{ZnSO}_4$ ,  $\text{CoSO}_4$ ,  $\text{K}_2\text{SO}_4$ ; and  $2\text{MgSO}_4$ ,  $\text{KRbSO}_4$ , have been prepared, all of which are octahedral or tetrahedral in form. With the exception of the last, which much resembles the magnesium potassium, and magnesium rubidium, salts in the freedom with which it crystallises, such mixed salts do not crystallise as well as those containing two metals only. Doubtless many other such mixed crystals might likewise be produced.

## II.—ANISOTROPIC SALTS.

The following sulphates have been fused together in the same molecular proportion as the preceding :

(1) Potassium sulphate, with the sulphates of beryllium, cadmium, copper, calcium, strontium, barium, and lead, respectively.

(2) Rubidium sulphate, with the sulphates of zinc, manganese, nickel, and cobalt, respectively.

(3) Cæsium sulphate, with the sulphates of magnesium, zinc, manganese, nickel, and cobalt, respectively.

(4) Magnesium sulphate, with thallium, lithium, sodium, and silver sulphates, respectively.

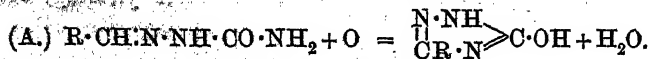
The resulting products are all of non-isometric crystallisation, as shown, in most cases by their external characters, and in all by their birefringence.\* While they have not, as yet, been examined in detail, it may be said that many of them afford no obvious indication of the two sulphates being otherwise than in uniform combination. More than one of the coloured products, however, show, by differences in colour, that they are not homogeneous, a fact which is not only pertinent to these particular cases, but also suggests caution in forming conclusions as to those in which absence of colour would make the recognition of two intercrystallised birefringent salts more difficult.

I propose experimenting further, with a view to the production of other double salts of the same general type.

## XXI.—C-Derivatives of Hydroxytriazole.

By GEORGE YOUNG, Ph.D., and ERNEST WITHAM, B.A., B.Sc.

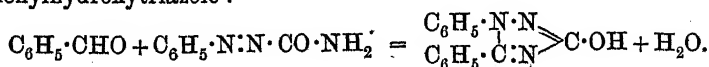
IN the following pages, we describe two methods of preparing C-derivatives of hydroxytriazole. The first consists in oxidising a semicarbazone, when action takes place according to the general equation :



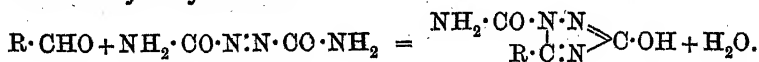
\* That containing rubidium and manganese is, in part, isotropic.

The hydroxytriazoles formed in this way might equally well be represented by the structural formula  $\begin{array}{c} \text{N} \text{---} \text{N} \\ \text{CR} \cdot \text{NH} \end{array} \text{>C} \cdot \text{OH}$ . By this reaction, we have prepared three hydroxytriazoles in which R is  $\text{C}_6\text{H}_5$ ,  $m\text{NO}_2 \cdot \text{C}_6\text{H}_4$ , and  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}$  respectively.

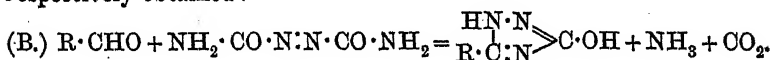
The second method is the condensation of an aromatic aldehyde with azodicarbamide. It has been previously shown by Young and Annable (Trans., 1897, 71, 201) that benzaldehyde condenses with phenylazocarbamide in the presence of ferrous chloride to form diphenylhydroxytriazole:



When starting this work, we hoped to find conditions under which aromatic aldehydes would condense with azodicarbamide to form carbamidohydroxytriazoles:



Our intention was to remove the carbamido-group by hydrolysis, with the object of obtaining, if possible, isomerides of the hydroxytriazoles prepared by action A. In the end we were able to condense benzaldehyde and *m*-nitrobenzaldehyde with azodicarbamide, but under the conditions of the reaction, the carbamido-group was split off, and phenyl- and *m*-nitrophenyl-hydroxytriazole were respectively obtained:



When R is the same group, the hydroxytriazole prepared by reaction A should be, from the structural formulæ, isomeric with the product of reaction B. We have compared the two phenylhydroxytriazoles and the two nitrophenylhydroxytriazoles formed by these two actions, as also the acetyl derivatives prepared from them, but have been quite unable to distinguish in any way the products of A from those of B. The melting points of the pairs of substances were compared directly by attaching two capillary tubes to the thermometer. Such comparisons were repeated until we had satisfied ourselves that we could not distinguish between the melting points of the two substances. In so far as the object of our work was to ascertain the possibility of distinguishing between position 3 and position 5 in the triazole ring when the N-hydrogen atom is present, the result must be regarded as altogether inconclusive. As the reactions by which the substances are prepared have to be carried out in alcohol at high temperatures under pressure, isomeric change might easily take place. On the

other hand, although the pairs of hydroxytriazoles which we have studied are so alike that we have found ourselves unable to distinguish the product of one method of preparation from the product of the other, we would not deny the possibility of their being isomeric and not really identical. One of us, in conjunction with Mr. W. H. Oates, has prepared by similar actions two N-methyl-C-phenylhydroxytriazoles which, although not quite identical in their properties, have been found to resemble each other so closely as to suggest that with methyl replaced by hydrogen, the differences might become so small as to escape detection. Unfortunately, the substances obtained by us do not lend themselves to crystallographical examination.

It is proposed to discuss this question of isomerism or identity and its relation to Knorr's work on the constitution of pyrazole in a future paper.

The products of the two reactions have the general properties of the hydroxytriazoles; they are weak acids, easily soluble in alkalis, forming red solutions, but at the same time are weak bases, being soluble in concentrated mineral acids. The ammonium salts dissociate when their aqueous solutions are warmed. The alkaline solutions do not reduce Fehling's solution.

It has been pointed out by Wedekind (*Ber.*, 1898, 31, 949) that in cyclic compounds containing both carbon and nitrogen the substitution of a group for C-hydrogen tends to raise the melting point, whilst the same group introduced in the place of N-hydrogen lowers the melting point. In agreement with this, the three C-derivatives of hydroxytriazole described in the following pages are substances of high melting point, and fuse at temperatures above 300°.



M. p. 273–274°.  
(Widman, *Ber.*, 1896,  
29, 1946.)



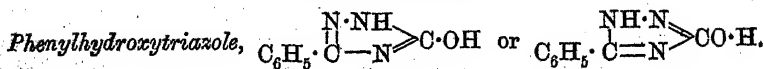
M. p. 288°.  
(Young, *Trans.*, 1895,  
67, 1063.)



M. p. 321–322°  
(This paper.)

M. p. 290° (Widman, *loc. cit.*)

#### EXPERIMENTAL.



A. *Preparation from Benzalsemicarbazone.*—Benzalsemicarbazone is not attacked by an alcoholic solution of ferric chloride even on prolonged boiling in a reflux apparatus, but when heated at higher temperatures under pressure, oxidation to phenylhydroxytriazole takes place. The best results were obtained by the use of slightly more than 1 molecular proportion of ferric chloride, and by heating at

125—130° for 1 hour. After cooling, there was only a very slight pressure in the tube. The alcohol was expelled by distillation with steam. On cooling the residue, the product crystallised out in scales, and was purified by solution in caustic soda and precipitation by sulphuric acid, and further by solution in aqueous ammonia and dissociation of the ammonium salt by boiling. The product formed white, crystalline scales which melted at 321—322°. The melting point was not altered by fractional crystallisation from alcohol.

0.1767 gave 0.3865 CO<sub>2</sub> and 0.0664 H<sub>2</sub>O. C=59.65; H=4.17.

0.1488 „ 33.2 c.c. moist nitrogen at 15° and 761 mm. N=26.15.

C<sub>8</sub>H<sub>7</sub>ON<sub>3</sub> requires C=59.62; H=4.34; N=26.09 per cent.

Phenylhydroxytriazole, prepared by this method, is easily soluble in hot alcohol, from which it is deposited on cooling as a white, crystalline powder. It is easily soluble in alkalis or in warm potassium carbonate solution, and the alkaline solutions do not reduce Fehling's solution or silver nitrate even on prolonged boiling. It dissolves on warming with concentrated hydrochloric acid, and is reprecipitated unchanged by the addition of water.

The solution of the ammonium salt yields, with silver nitrate, a heavy, white precipitate, the composition of which depends on the conditions of precipitation.

Phenylhydroxytriazole was dissolved in hot aqueous ammonia, and the solution kept hot until separation of the hydroxytriazole had commenced; it was then cooled and filtered, the filtrate containing just sufficient ammonia to keep the hydroxytriazole dissolved. To this a cold dilute solution of silver nitrate was added so long as precipitation took place. The precipitate was collected, washed, finally with alcohol and ether, and dried at 110° until of constant weight. A silver determination showed the dried precipitate to be a *mono-silver* salt.

0.5895 gave 0.2395 Ag. Ag=40.63.

C<sub>8</sub>H<sub>6</sub>ON<sub>3</sub>Ag requires Ag=40.30 per cent.

When, on the other hand, the phenylhydroxytriazole was dissolved in excess of ammonia, the hot ammoniacal solution poured into the solution of silver nitrate, and the excess of ammonia driven off by heating, the resulting precipitate, after being dried at 110°, yielded on analysis an amount of silver corresponding to that required by a *di-silver* salt.

1.6589 gave 0.9481 Ag. Ag=57.15.

C<sub>8</sub>H<sub>6</sub>ON<sub>3</sub>Ag<sub>2</sub> requires Ag=57.60 per cent.

If the above conditions are not observed, the precipitate consists of

a mixture of the two salts. In one case when the mono-silver salt was allowed to stand in contact with an ammoniacal solution of silver nitrate, the analysis showed that a considerable amount had been converted into the di-silver salt.

0.9877 gave 0.4369 Ag. Ag = 44.23 per cent.

When phenylhydroxytriazole is heated in a dry bulb-tube, it sublimes, and at the same time undergoes charring, accompanied by an odour of benzoic acid. A *monoacetyl* derivative,  $C_6H_5 \cdot C_2HON_3 \cdot CO \cdot CH_3$ , is formed by boiling phenylhydroxytriazole with acetic anhydride and sodium acetate. It is easily soluble in hot alcohol, but only slightly so in ether, and crystallises from alcohol in shining, colourless, flat needles which melt at  $248^\circ$ . It is easily hydrolysed by boiling with alcoholic potash.

0.1741 gave 30.0 c.c. moist nitrogen at  $11^\circ$  and 768 mm. N = 20.75.

$C_{10}H_9O_2N_3$  requires N = 20.68 per cent.

*B. Preparation from Azodicarbamide.*—Azodicarbamide and benzaldehyde, in molecular proportion, were heated with ferrous chloride and alcohol in a sealed tube at  $130^\circ$  for 1 hour. There was a high pressure in the cooled tube. The contents were distilled with steam to remove alcohol and excess of benzaldehyde. The crystalline product was found to consist of phenylhydroxytriazole and hydrazodicarbamide, the latter being removed by treatment with boiling water, and the phenylhydroxytriazole purified in the manner described on p. 227.

0.1777 gave 0.3872  $CO_2$  and 0.0685  $H_2O$ . C = 59.42; H = 4.28.

0.1481 „ 0.3231  $CO_2$  „ 0.0543  $H_2O$ . C = 59.49; H = 4.07.

0.1456 „ 34.2 c.c. moist nitrogen at  $15.5^\circ$  and 739 mm. N = 26.67.

$C_8H_7ON_3$  requires C = 59.62; H = 4.34; N = 26.09 per cent.

The phenylhydroxytriazole, prepared by this method, melted at  $321$ — $322^\circ$ , and had the same properties as those described for the phenylhydroxytriazole prepared from benzalsemicarbazone. The silver salts and the acetyl derivative were prepared in the same way as those described above, and could not be distinguished from them. We confine ourselves to giving only the analytical data.

Mono-silver salt, dried at  $110^\circ$ .

1.2631 gave 0.5122 Ag. Ag = 40.55 per cent.

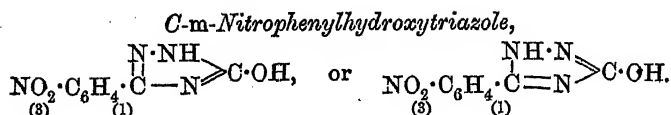
Di-silver salt, dried at  $110^\circ$ .

1.0756 gave 0.6161 Ag. Ag = 57.28 per cent.

Acetyl derivative.

0.1776 gave 31.1 c.c. moist nitrogen at  $11^\circ$  and 758 mm. N = 20.81 per cent.





*m*-Nitrophenylhydroxytriazole was prepared in the same manner as phenylhydroxytriazole, on the one hand, from *m*-nitrobenzalsemicarbazone (Thiele, *Annalen*, 1894, 283, 25) by oxidation with ferric chloride at 130—140°, and, on the other hand, by condensation of *m*-nitrobenzaldehyde with azodicarbamide in the presence of ferrous chloride and alcohol at 130—135°.

We were unable to distinguish between the two products. One description will therefore suffice for both, as also for the corresponding silver salts and acetyl derivatives. Analyses marked 'A' are those of the products from the semicarbazone, those marked 'B' belong to the azodicarbamide series.

*m*-Nitrophenylhydroxytriazole crystallises from dilute alcohol in slightly yellow nodules, from glacial acetic acid in microscopic plates or needles, and melts at 304°. It is fairly soluble in hot alcohol, but insoluble in water, ether, and benzene. It is easily soluble in alkalis or in a warm aqueous solution of potassium carbonate, and the alkaline solutions do not reduce Fehling's solution or silver nitrate. On boiling the ammoniacal solution, the hydroxytriazole separates out as a crystalline crust, and in this way may be readily purified. *m*-Nitrophenylhydroxytriazole is easily soluble in hot concentrated hydrochloric acid, and on dilution is reprecipitated unchanged. If the concentrated hydrochloric acid solution is cooled, the hydrochloride of the hydroxytriazole separates out. It is very unstable and commences to dissociate so soon as it is removed from the mother liquor. ‡

A. 0.1770 gave 0.3031 CO<sub>2</sub> and 0.0460 H<sub>2</sub>O. C=46.70; H=2.88.

B. 0.1651 „ 0.2831 CO<sub>2</sub> „ 0.0448 H<sub>2</sub>O. C=46.79; H=3.02.

A. 0.1780 „ 40.2 c.c. moist nitrogen at 11° and 764 mm. N=27.06.

B. 0.1241 „ 28.5 c.c. „ „ 15° „ 766 mm. N=27.13.

C<sub>8</sub>H<sub>6</sub>O<sub>3</sub>N<sub>4</sub> requires C=46.60; H=2.90; N=27.18 per cent.

The mono- and di-silver salts were prepared in exactly the same manner as the corresponding salts of phenylhydroxytriazole. They were dried at 110° to a constant weight before analysis.

The *mono-silver* salt formed a golden-yellow precipitate, and became brown on drying.

A. 1.1424 gave 0.3953 Ag. Ag=34.60.

B. 1.2078 „ 0.4261 Ag. Ag=35.27.

C<sub>8</sub>H<sub>5</sub>O<sub>3</sub>N<sub>4</sub>Ag requires Ag=34.50 per cent.

The *di-silver* salt, when freshly precipitated, had a bright yellow colour, which changed on drying to a deep yellowish-red.

A. 1.2672 gave 0.6462 Ag. Ag = 50.99.

B. 1.3566 „ 0.6867 Ag. Ag = 50.62.

$C_8H_4O_3N_4Ag_2$  requires Ag = 51.43 per cent.

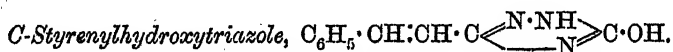
The acetyl derivatives were made by boiling the nitrophenylhydroxytriazoles with acetic anhydride and sodium acetate. From both a *monoacetyl* derivative,  $NO_2 \cdot C_6H_4 \cdot CHON_3 \cdot CO \cdot CH_3$ , was formed, which crystallised from dilute alcohol as a yellow, crystalline powder melting at 261–262°.

A. 0.1850 gave 37.0 c.c. moist nitrogen at 20° and 757 mm. N = 22.78.

B. 0.1792 „ 34.9 c.c. „ „ 14° „ 755 mm. N = 22.75.

$C_{10}H_8O_4N_4$  requires N = 22.58 per cent.

The acetyl derivative is easily hydrolysed by boiling with alkalis. On acidification of the alkaline solution, the *m*-nitrophenylhydroxytriazole, melting at 304°, is precipitated.



We have prepared C-styrenylhydroxytriazole by one method only, namely, by oxidation of cinnamalsemicarbazone.

*Cinnamalsemicarbazone*,  $C_6H_5 \cdot CH : CH \cdot CH : N \cdot NH \cdot CO \cdot NH_2$ , was prepared by Thiele's method (*loc. cit.*) for the formation of aromatic semicarbazones. It can be recrystallised from boiling water, and then forms slightly yellow, shining plates, which melt at 215–216°. It is easily soluble in warm alcohol, but less so in cold alcohol or ether.

0.1523 gave 0.3537  $CO_2$  and 0.0808  $H_2O$ . C = 63.34; H = 5.89.

0.1740 „ 34.4 c.c. moist nitrogen at 20° and 755.6 mm. N = 22.47.

$C_{10}H_{11}ON_3$  requires C = 63.49; H = 5.82; N = 22.22 per cent.

Cinnamalsemicarbazone was oxidised to styrenylhydroxytriazole by heating with ferric chloride and alcohol in a sealed tube at 135–140° for one hour. The product smelt strongly of cinnamaldehyde, which was removed along with the alcohol by distillation with steam. The residue was filtered hot, and the precipitate recrystallised from alcohol, and finally from glacial acetic acid. The product so obtained melted at 311–312°, and, on analysis, gave figures agreeing with those required by styrenylhydroxytriazole.

0.1901 gave 0.4458  $CO_2$  and 0.0855  $H_2O$ . C = 63.96; H = 4.99.

0.1938 „ 36.5 c.c. moist nitrogen at 11° and 760 mm. N = 22.52.

$C_{10}H_9ON_3$  requires C = 64.17; H = 4.81; N = 22.46 per cent.

Styrenylhydroxytriazole is readily soluble in alcohol, but only very

slightly so in benzene—from which it may be precipitated by the addition of light petroleum—and insoluble in water or ether. It is readily soluble in alkalis, and the alkaline solutions do not reduce Fehling's solution. The ammoniacal solution, on warming, deposits the hydroxytriazole in slightly yellow, crystalline scales. It dissolves in concentrated hydrochloric acid, and in warm glacial acetic acid, from which it is deposited, on cooling, in microscopic plates.

Styrenylhydroxytriazole forms two silver salts in the manner and under the same conditions as phenylhydroxytriazole. The *mono-silver* salt is formed as a faintly yellow precipitate which darkens slightly when dried at 100°.

0.9788 gave 0.3628 Ag.  $\text{Ag} = 37.06$ .

$\text{C}_{10}\text{H}_8\text{ON}_3\text{Ag}$  requires  $\text{Ag} = 36.73$  per cent.

The *di-silver* salt was of a deeper yellow, and also darkened slightly when dried at 100°.

1.2359 gave 0.6630 Ag.  $\text{Ag} = 53.64$ .

$\text{C}_{10}\text{H}_7\text{ON}_3\text{Ag}_2$  requires  $\text{Ag} = 53.86$  per cent.

When styrenylhydroxytriazole is boiled with acetic anhydride and sodium acetate, the product consists of a mixture of two acetyl derivatives which, by treatment with ether and with light petroleum, can be easily separated into a monoacetyl derivative melting at 241—242°, and a diacetyl derivative melting at 137—138°.

The *monoacetyl* derivative,  $\text{C}_{10}\text{H}_8\text{ON}_3\cdot\text{CO}\cdot\text{CH}_3$ , is easily soluble in alcohol, but only sparingly so in boiling ether, and almost insoluble in boiling light petroleum. It crystallises from dilute alcohol in small, white needles.

0.1496 gave 24.3 c.c. moist nitrogen at 16° and 743 mm.  $\text{N} = 18.50$ .

$\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}_3$  requires  $\text{N} = 18.34$  per cent.

The *diacetyl* derivative,  $\text{C}_{10}\text{H}_7\text{ON}_3(\text{C}_2\text{H}_3\text{O})_2$ , is easily soluble in alcohol or boiling ether, and fairly so in cold ether or boiling light petroleum. From the last solvent, it crystallises in colourless nodules, but from dilute alcohol in small needles.

0.1582 gave 21.3 c.c. moist nitrogen at 14.5° and 756 mm.  $\text{N} = 15.72$ .

$\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}_3$  requires  $\text{N} = 15.49$  per cent.

Both acetyl derivatives are easily hydrolysed by alkalis to styrenylhydroxytriazole melting at 311—312°.

We take this opportunity of thanking Mr. Fred. Ibbotson, B.Sc., for his assistance in the early stages of the work.

XXII.—*Note on Volhard's Method for the Assay of Silver Bullion.*

By THOMAS KIRKE ROSE, D.Sc.

THE method of estimating silver by means of ammonium thiocyanate described by Volhard (*Chem. News*, 1878, 37, 77) gives results with pure silver which are said by van Riemsdijk to be accurate to 0.25 part per 1000 (*Algemeen Verslag. Munt-Collegie*, 1878; Appendix, 38).

The general practice appears to be, after adding the normal solution, to make successive additions of decinormal solution, each sufficient to precipitate 0.25 milligram of silver, the reason assigned by van Riemsdijk being that an appreciable colour cannot be obtained without an excess of about that amount of the thiocyanate solution.

A limit of accuracy of less than 0.1 per 1000 of silver can, however, be obtained in testing the purity of fine silver by taking the following precautions.

One gram of silver is dissolved in a slight excess of dilute nitric acid in a bottle fitted with a stopper and subjected to prolonged heating to expel all traces of nitrous acid. 100 c.c. of normal solution of ammonium thiocyanate are added from a burette found by repeated trials to deliver a constant quantity of solution, the variation in the amount being less than 0.0025 c.c. The strength of the normal solution is adjusted so that from 0.5 to 1.0 milligram of silver remains in solution. The bottle is then well shaken and its contents immediately filtered. The precipitate needs very little washing, as the loss of even 2 or 3 c.c. of the liquid would not affect the result. Five c.c. of a saturated solution of iron alum decolorised by nitric acid, or better still of ferric nitrate, are then added, and the decinormal solution of thiocyanate run in drop by drop. When all the silver is precipitated, the addition of one drop (0.05 c.c. equivalent to 0.05 milligram of silver) of the decinormal solution converts the colourless silver solution to one of a pale straw colour. An additional weight of 0.1 milligram in the silver originally taken is readily recognised in the final reading. No time is saved by omitting to filter off the main bulk of the precipitate, as it must then be allowed to settle after each addition of decinormal solution, and the end reaction is not observed so easily, although quite distinct when 0.25 c.c. is added at a time.

Similar results can be obtained for alloys containing less than 50 parts of copper per 1000 of silver. The colour of the copper nitrate, however, masks the result if more than this amount is present. In that event, the light straw colour is not reached until the real limit is passed, and it is necessary to use checks of pure silver with the addition

of about the same amount of copper as in the alloys to be assayed. With this precaution, fairly good approximate assays can be obtained with alloys as low as 300 fine as indicated by Volhard.

This method is less liable to error, although far less rapid, than the Gay Lussac method as ordinarily practised in Mints, the limit of accuracy of which is 0.2 to 0.3 per 1000. It has been used at the Royal Mint in comparing the Silver Trial Plates now in course of preparation with those made in 1873.

ROYAL MINT, LONDON.

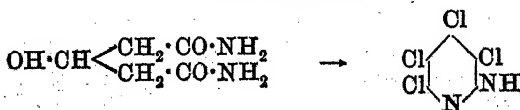
### XXIII.—*The Chlorine Derivatives of Pyridine. Part V.* *The Constitution of Citrazinic Acid. Formation* *of 2 : 6-Dichloropyridine and 2 : 6-Diiodoisonicotinic* *Acid.*

By W. J. SELL, M.A., F.I.C., and F. W. DOOTSON, M.A.

THE formation of citrazinic acid from citric acid renders it very probable that the hydroxyl groups in the former substance occupy the 2 : 6-positions relatively to the nitrogen, but hitherto no direct evidence of this has been obtained. The importance of the derivatives of the acid, definite knowledge of whose constitution depends upon the correct orientation of the radicles in citrazinic acid, makes it desirable that we should possess further evidence on this point. The problem has previously been approached in several ways, but owing to the unexpected stability of dichloroisonicotinic acid, the results have been unsatisfactory.

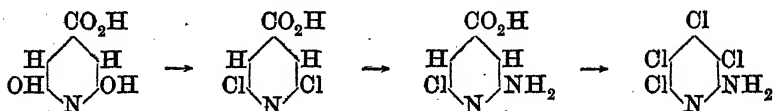
It has been pointed out in an earlier paper (Trans., 1897, 71, 1082) that hydrogen atoms attached to a pyridine nucleus can be replaced with ease by chlorine by means of phosphorus pentachloride. It is here and elsewhere further shown that in aminopyridines the amino-group is not attacked by this reagent under the same conditions. Aminopyridines invariably yield aminochloropyridines with phosphorus pentachloride at a temperature of about 220°.

$\beta$ -Hydroxyglutaramide was prepared and treated with phosphorus pentachloride. The product of the reaction was mainly tetrachloroaminopyridine fusing at 174—175° (uncorr.), in which the amino-group should be adjacent to the nitrogen, thus :



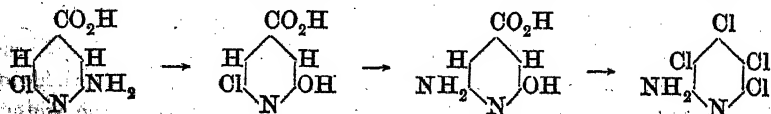
a view which is supported by other considerations (compare *Trans.*, 1898, 73, 779).

By the action of phosphorus pentachloride on citrazinic acid, dichloroisonicotinic acid has been obtained (*Ber.*, 1884, 17, 2694; *Trans.*, 1897, 71, 1069), and on fusion of the latter with caustic soda or potash, citrazinic acid is reformed (*Trans.*, 1897, 71, 1075), so that presumably there has been no intramolecular migration of atoms. Dichloroisonicotinic acid, by its interaction with ammonia, yields chloroaminoisonicotinic acid, and the latter, on treatment with phosphorus pentachloride, loses its carboxyl group, yielding a tetrachloroaminopyridine fusing at 174—175° (uncorr.), identical with the substance obtained from  $\beta$ -hydroxyglutaric acid, as described above. These changes may be represented thus :



By these reactions, one of the OH groups is shown to be in the 2-position relatively to the nitrogen.

That both hydroxyl groups in citrazinic acid occupy the same relative position in the molecule is demonstrated by the following series of substitutions. Chloroaminoisonicotinic acid was treated with nitrous acid by a modification of Bouveault's method (*Trans.*, 1898, 73, 781) and chlorohydroxyisonicotinic acid obtained. This substance is identical with the product of the action of aqueous caustic soda or potash on dichloroisonicotinic acid or its ester (*Trans.*, 1897, 71, 1075), as was shown by its general properties, and by the fusing point of the methyl ester. The acid, on treatment with aqueous ammonia in sealed tubes, yielded a compound free from chlorine, which proved to be aminohydroxyisonicotinic acid, and by its interaction with phosphorus pentachloride the latter was converted into tetrachloro-2-aminopyridine, melting at 174—175° (uncorr.), also identical with that mentioned above. These changes are thus shown :



It may here be pointed out that, as the same tetrachloroaminopyridine has been prepared by the action of ammonia on pentachloropyridine (*Trans.*, 1898, 73, 779), there can be no question of the amino-group having been attacked by phosphorus pentachloride in the reactions shown above.

Hofmann and Behrmann have already shown (*Ber.*, 1884 17, 2696) that dichloroisonicotinic acid is reduced by hydriodic acid in sealed tubes to isonicotinic acid. In repeating this experiment, it was found that when dichloroisonicotinic acid was boiled with strong hydriodic acid in open vessels, a substitution, and not a reduction, takes place, the product being 2 : 6-diiodoisonicotinic acid.

The silver salt of dichloroisonicotinic acid, on being gently heated in a current of carbon dioxide in the manner described by Königs and Körner (*Ber.*, 1883, 16, 2153), yields a dichloropyridine, which sublimes in colourless, feathery scales, and after crystallisation from dilute alcohol melts at 87—88° (uncorr.). This compound is identical with the dichloropyridine obtained by the action of phosphorus pentachloride on dry pyridine (*Trans.*, 1898, 73, 438). Its non-basic character is in marked contrast to the basic properties of the only isomeric derivative so far described, and of certain of the more highly chlorinated derivatives of pyridine—a fact which supports the view held as to its constitution (compare this vol., 1.)

#### EXPERIMENTAL.

##### *Tetrachloro-2-aminopyridine from $\beta$ -Hydroxyglutaramide.*

On the authority of Anschütz (*Richter's Organische Chemie*, Ed. 1898, ii, 573), it is stated that  $\beta$ -hydroxyglutaramide, on treatment with phosphorus pentachloride, yields trichloro-2-aminopyridine melting at 144—145°. In view of the general behaviour of this class of compounds, it seemed probable that the remaining hydrogen atom of the nucleus might be replaced by chlorine without difficulty by means of phosphorus pentachloride at a higher temperature. As no record could be found of the experiments on which the statement of Anschütz is based, the operation was carried out as follows.

Diethyl  $\beta$ -hydroxyglutarate was poured into a large excess of strong aqueous ammonia, in which it gradually but completely dissolved in the cold. After standing for two days, the water and excess of ammonia were removed in a vacuum over sulphuric acid, the semi-solid mass drained by the aid of the filter pump, and washed with small quantities of spirit, in which the diamide is only sparingly soluble. The nearly colourless product was heated with excess of phosphorus pentachloride in a reflux apparatus for 3—4 hours, then poured into water, and finally distilled with steam. The colourless crystals filtered off from the distillate were frequently crystallised from dilute alcohol, and consisted chiefly of a compound melting at 143—144° (uncorr.); a small quantity only of pentachloropyridine being obtained. The substance melting at 143—144°, on further treatment with excess of phosphorus pentachloride (2 mols.) in sealed

tubes at 220—230° and subsequent distillation with steam, yielded tetrachloroaminopyridine, which, after purification from alcohol, melted at 174—175° (uncorr.). On analysis:

0.1067 gave 0.2660 AgCl. Cl = 61.34.

0.1012 „ 10.16 c.c. nitrogen at 15° and 770 mm. N = 11.91.

$C_5H_2N_2Cl_4$  requires Cl = 61.14. N = 12.06 per cent.

This compound crystallises from alcohol in long needles and is soluble in the usual organic solvents. Water and dilute mineral acids dissolve it slightly on boiling. It is easily soluble in cold strong sulphuric acid, and is reprecipitated on diluting. Strong nitric acid decomposes it at the ordinary temperature. It is not acted on by cold alkalis, and volatilises only slowly in steam.

*Tetrachloro-2-aminopyridine from Citrazinic Acid.*

Chloroaminoisonicotinic acid, prepared from citrazinic acid (*Ber.*, 1884, 17, 2694; *Trans.*, 1897, 71, 1075), was heated in sealed tubes at 210—220° for 4 hours with excess of phosphorus pentachloride. The product was poured into water and distilled with steam. The light, feathery crystals from the distillate, on purification from spirit, melted at 174—175° (uncorr.). On analysis:

0.1992 gave 12.5 c.c. nitrogen at 17° and 750 mm. N = 12.01.

0.0761 „ 0.1877 AgCl. Cl = 60.99.

$C_5H_2N_2Cl_4$  requires Cl = 61.14. N = 12.06 per cent.

The properties of the compound thus prepared agree in every way with those of tetrachloro-2-aminopyridine described above.

*6-Chloro-2-hydroxyisonicotinic Acid from 6-Chloro-2-aminoisonicotinic Acid.*

Chloroaminoisonicotinic acid, dissolved in strong sulphuric acid, was mixed with a slight excess of sulphuric acid previously saturated with nitrous fumes. After heating for several minutes on the water-bath, the solution was slowly diluted, again heated on the water-bath, and finally poured into water. The precipitate, after purification by crystallisation from alcohol, was converted into the methyl ester, which, when recrystallised from spirit, melted at 189—190° (uncorr.). On analysis:

0.0733 gave 0.1202  $CO_2$  and 0.021  $H_2O$ . C = 44.72; H = 3.19.

0.1622 „ 10.3 c.c. nitrogen at 16.4° and 771.6 mm. N = 7.63.

0.0965 „ 0.0735 AgCl. Cl = 18.60.

$C_7H_5O_3NCl$  requires C = 44.80; H = 3.20; Cl = 18.80; N = 7.46 per cent.



The acid is easily soluble in hot alcohol and in alkalis, sparingly so in boiling water and in ether, and insoluble in cold water and in dilute mineral acids. The compound prepared in this way is identical with the product of the action of caustic soda or potash on dichloroisonicotinic acid (*loc. cit.*), as is shown by the fusing point of the methyl ester.

*6-Amino-2-hydroxyisonicotinic Acid from 6-Chloro-2-hydroxyisonicotinic Acid.*

Chlorohydroxyisonicotinic acid, prepared as described above, was heated in sealed tubes for 4 hours at 170—180° with a large excess of strong aqueous ammonia. When cool, the contents of the tubes were diluted, acidified with hydrochloric or sulphuric acid, and any unchanged chlorohydroxyisonicotinic acid filtered off. The latter may also be easily removed by boiling with alcohol, in which it dissolves freely, whilst the solubility of aminohydroxyisonicotinic acid in alcohol is very small. After dissolving in alkali and reprecipitating by neutralisation with hydrochloric acid, a compound free from chlorine was obtained. On analysis :

0.1560 gave 23.9 c.c. nitrogen at 15° and 740 mm.  $N = 17.77$ .

$C_6H_6O_3N_2$  requires  $N = 18.18$  per cent.

This compound chars without fusing. It is very sparingly soluble in the usual organic solvents and in boiling water. Alkalis and dilute mineral acids dissolve it easily, and from these it is reprecipitated on neutralisation. The *ammonium* salt is dissociated when its solution is evaporated to dryness. The *silver* salt, obtained by the addition of silver nitrate to the ammonium salt in solution, crystallises in yellowish needles which blacken on warming. The *lead* salt is an insoluble colloid; the *calcium* and *barium* salts are soluble.

*Tetrachloro-6-aminopyridine from 6-Amino-2-hydroxyisonicotinic Acid.*

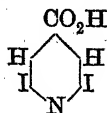
Aminohydroxyisonicotinic acid was heated in sealed tubes at 230—240° for several hours with excess of phosphorus pentachloride. On cooling, the product was poured into water, distilled with steam, and purified in the manner already described. The recrystallised substance melted at 174—175° (uncorr.). On analysis :

0.0602 gave 0.1495 AgCl.  $Cl = 61.40$ .

$C_5H_2N_2Cl_4$  requires  $Cl = 61.14$  per cent.

The product obtained thus coincides in every way with 2-amino-tetrachloropyridine prepared by any of the methods already described.

## 2:6-Diiodoisonicotinic Acid from 2:6-Dichloroisonicotinic Acid,



Dichloroisonicotinic acid was covered with sufficient fuming hydriodic acid to dissolve it completely on warming, and boiled in a reflux apparatus for half an hour. At the end of that time a copious, heavy, sand-like precipitate separated out, and was removed by filtration through a platinum cone, whilst a further quantity was obtained on largely diluting the filtrate. After recrystallising a few times from dilute alcohol, the acid melted at  $195-196^{\circ}$  (uncorr.). On analysis:

0.1393 gave 0.1005  $\text{CO}_2$  and 0.0105  $\text{H}_2\text{O}$ .  $\text{C} = 19.67$ ;  $\text{H} = 0.85$ .

0.1485 „ 0.1075  $\text{CO}_2$  „ 0.0115  $\text{H}_2\text{O}$ .  $\text{C} = 19.70$ ;  $\text{H} = 0.86$ .

0.1020 „ 0.1270  $\text{AgI}$ .  $\text{I} = 67.32$ .

$\text{C}_6\text{H}_3\text{O}_2\text{NI}_2$  requires  $\text{C} = 19.23$ ;  $\text{H} = 0.80$ ;  $\text{I} = 67.11$  per cent.

This substance is more easily dissolved by alcohol than the corresponding chloro-derivative. Alkalis dissolve it freely, and from the solution it is reprecipitated by dilute acids, in which it is practically insoluble. Strong sulphuric or nitric acid dissolves it in the cold, and, as was shown by an iodine determination, it may be boiled with strong nitric acid without change. The *ammonium* salt crystallises in long needles, and is only sparingly soluble in cold water; the *sodium* and *potassium* salts are also sparingly soluble, and crystallise in slender, colourless needles. The *calcium* salt is moderately soluble in boiling water. The *barium* and *lead* salts are colloidal substances, which could not be obtained crystalline, although easily soluble in boiling water, and only sparingly so in cold. The *ferric* salt is an insoluble, yellow powder. The *copper* salt crystallises from water in beautiful, blue needles. The *cadmium* and *gold* salts are readily soluble in boiling, but insoluble or nearly so in cold water.

## 2:6-Dichloropyridine from Dichloroisonicotinic Acid,

The addition of silver nitrate solution to a solution of ammonium dichloroisonicotinate yields a well-defined, crystalline silver salt, which may be crystallised unchanged from boiling water, a fact which has been made use of in the separation of dichloroisonicotinic acid from tetrachloroisonicotinic acid, the latter being invariably present in preparations of dichloroisonicotinic acid by any of the methods hitherto described.

The silver salt, purified and dried at  $100^{\circ}$ , was gently heated in a current of carbon dioxide. The light, feathery sublimate was collected and recrystallised several times from dilute alcohol, when it was obtained in colourless, pearly scales melting at  $87-88^{\circ}$  (uncorr.). On analysis:

0.1240 gave 10.3 c.c. nitrogen at  $17^{\circ}$  and 770 mm.  $N = 9.61$ ,

0.1260 „ 0.2436 AgCl.  $Cl = 47.93$ .

$C_5H_3NCl_2$  requires  $N = 9.46$ ;  $Cl = 47.97$  per cent.

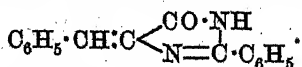
This compound has already been isolated from the product of the interaction of phosphorus pentachloride on pyridine (Trans., 1898, 73, 437). The properties of the substance obtained in the manner shown above agree entirely with those already described.

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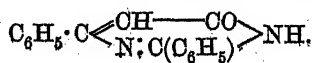
## XXIV.—*The Formation of Heterocyclic Compounds.*

By SIEGFRIED RUHEMANN and H. E. STAPLETON, Scholar of St. John's College, Oxford.

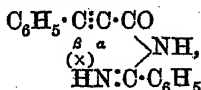
THE research on the formation of  $\alpha$ -pyrone compounds (Ruhemann, Trans., 1899, 75, 245, and 411), by the action of ethyl phenylpropiolate on the sodium derivatives of  $\beta$ -diketones and the ethyl esters of  $\beta$ -ketonic acids, induced one of us and A. V. Cunningham to examine the behaviour of organic bases towards the ethyl esters of the acids of the acetylene series, with the view of ascertaining whether in those cases also additive substances were formed which subsequently lost alcohol, and condensed to heterocyclic compounds. A few months ago (Trans., 1899, 75, 954) we published the first part of our investigations in this direction, and were able to show that by the interaction of benzamidine and ethyl phenylpropiolate a cyclic compound was produced. The constitution of this substance we represented by the symbol,



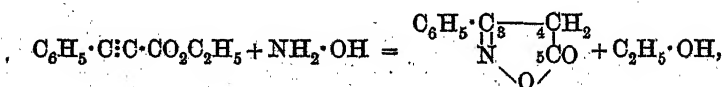
A closer examination of the reaction has led the authors of the present paper to the discovery of the following interesting fact. At the ordinary temperature, benzalphenylglyoxalidone is formed almost exclusively, but on digesting the mixture of the ethyl ester and the amidine on the water-bath, besides this substance another is produced which has been identified as *diphenylpyrimidone*,



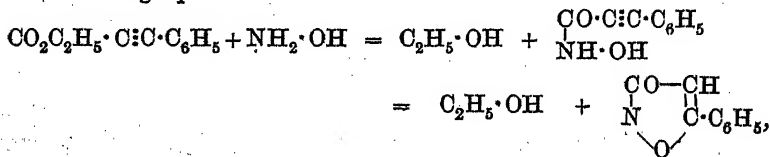
This result can readily be explained on the assumption that benzamidine and ethyl phenylpropiolate first react with formation of the benzamidine of phenylpropionic acid,



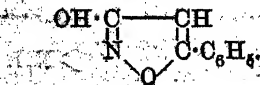
and that subsequently, according to the conditions which exist, the hydrogen atom (x) unites either to the  $\beta$ - or the  $\alpha$ -carbon atom, in the first case a 5-membered, and in the second a 6-membered ring being produced. The view expressed above as to the intermediate phase of the reaction between benzamidine and ethyl phenylpropiolate is also supported by the results of the study of the behaviour of other bases towards ethyl phenylpropiolate. It had been previously assumed that addition of the base to the ester would precede the ring-formation, which would be effected by subsequent removal of alcohol, and we were led to this assumption by the fact that ethyl phenylpropiolate forms additive products, not only with the sodium derivatives of ethyl malonate and ketonic compounds, but also with secondary bases such as diethylamine and piperidine. Since the action of hydroxylamine on ethyl phenylpropiolate does not yield 3-phenyl-5-isoxazolone according to the equation,



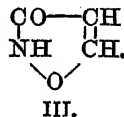
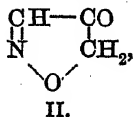
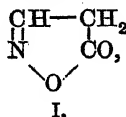
it was supposed that the product of the reaction was phenylpropiolohydroxamic acid,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \beta \\ \text{(\times)} \end{array} \text{C} \begin{array}{l} \alpha \\ \text{N} \cdot \text{OH} \end{array} \cdot \text{OH}$ . A closer investigation of this substance has, however, proved it to be a cyclic compound isomeric with 3-phenyl-5-isoxazolone. Its formation can only be interpreted by assuming that the action takes place in the manner expressed by the following equation :



The compound appears, therefore, as 5-phenyl-3-isoxazolone, or as its tautomeride, 5-phenyl-3-hydroxyisoxazole,

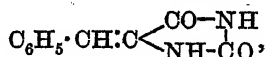


From isoxazole, or the dihydroxyisoxazoles, there may be derived three isoxazolones, which are represented by the following symbols:



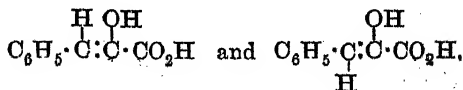
The first isoxazolones which were obtained belonged to type I, and have been studied especially by Claisen (*Ber.*, 1891, 24, 141), whilst some derivatives of 4-isoxazolone (II) were prepared by Abenius and Söderbaum (*Ber.*, 1892, 25, 3468). The compound which is formed by the interaction of hydroxylamine and ethyl phenylpropiolate is therefore to be regarded as a 3-substitution product of type III.

The conclusion arrived at with regard to the mode of the interaction of benzamidine and hydroxylamine with ethyl phenylpropiolate induced us also to re-examine the product which is formed on allowing a mixture of alcoholic solutions of sodium ethoxide, urea, and ethyl phenylpropiolate to stand at the ordinary temperature. This substance, which had been regarded before by one of us and A. V. Cunningham (*loc. cit.*) as the ureide of the formula  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_5$ , we find, however, to be a cyclic compound. Its constitution is undoubtedly to be expressed by the symbol,



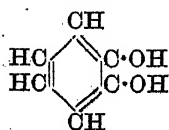
which characterises it as *benzalhydantoin*. This view is supported by the following facts: The substance, as mentioned previously, has acidic properties, dissolving freely in caustic potash. On boiling the alkaline solution, the odour of benzaldehyde is first perceptible, then ammonia is evolved, and finally an acid results, which we have found to be identical with Plöchl's "phenylglycidic acid" (*Ber.*, 1883, 16, 2817). This acid, which has since been obtained by Wislicenus from ethyl phenylxaloacetate (*Ber.*, 1887, 20, 591), has undoubtedly either the formula  $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , or  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H}$ . Although E. Erlenmeyer, jun. (*Annalen*, 1892, 271, 137), assigned to the acid the first formula, yet the second, which characterises it as  $\alpha$ -hydroxy-cinnamic acid, would also agree with the behaviour of the acid as described by him. The mode of its formation, and its relation to the

isomeride, phenylglycidic acid,  $\text{C}_6\text{H}_5 \cdot \text{CH} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CH}-\text{CH} \end{array} \cdot \text{CO}_2\text{H}$ , would thus find a ready explanation. This formula indicates the probable existence of two stereoisomeric forms,

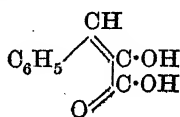
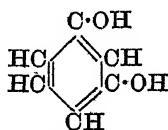


The first grouping could readily change into phenylglycidic acid, whilst the second might be expected to be the more stable. Moreover, the formation of phenylglycidic acid takes place by the action of cold caustic potash on  $\alpha$ -chlorophenyllactic acid, that of  $\alpha$ -hydroxycinnamic acid, on the other hand, under the influence of the boiling reagent from compounds of the cinnamyl series. These facts are in full agreement with the researches of Fittig and his pupils on the transformation of unsaturated acids into their stereoisomerides, and suggest that boiling caustic potash would partially change phenylglycidic acid into  $\alpha$ -hydroxycinnamic acid.

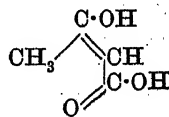
The fact that ferric chloride gives a green colour with  $\alpha$ -hydroxycinnamic acid (p. 246) whilst it gives a violet with esters of  $\beta$ -ketonic acids, such as ethyl acetoacetate, seems to indicate that the structure of the former is similar to that of catechol, just as the structure of acetoacetic acid is similar to that of resorcinol. This similarity is shown by the formulæ:



Catechol.

 $\alpha$ -Hydroxycinnamic acid.

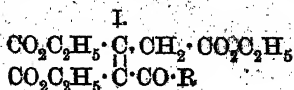
Resorcinol.



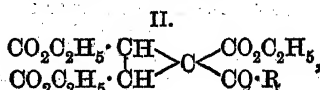
Acetoacetic acid.

Thiourea and guanidine react with ethyl phenylpropionate in a manner analogous to urea and yield respectively *benzalthiohydantoin* and *benzalimidohydantoin*. These substances are similarly decomposed by caustic potash, and yield  $\alpha$ -hydroxycinnamic acid. The destruction of the ring takes place in these cases with the same readiness, and is accompanied by the production of benzaldehyde. Benzalphenylglyoxalidone, on the other hand, is more stable, only partial decomposition being effected by boiling with the alkali, but a small quantity of the hydroxy-acid is certainly formed.

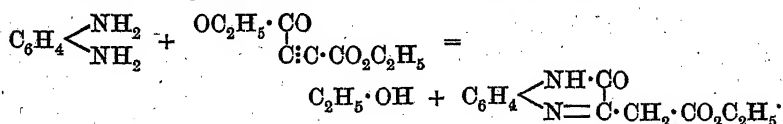
Besides the record of our work in the direction indicated above, this communication contains the results at which we have arrived, up to the present, by using ethyl acetylenedicarboxylate instead of ethyl phenylpropionate. The study of the action of organic bases on this salt appeared to us to be of especial interest, since it had been found (Ruhemann and Cunningham, Trans., 1899, 75, 784) that  $\alpha$ -pyrone derivatives do not result from its union with the ethyl esters of  $\beta$ -ketonic acids. This fact led to the conclusion that both hydrogen atoms of the  $\text{CH}_2$  group of the ketonic compound play a part in the reaction. Of the two expressions (R denoting  $\text{CH}_3$  or  $\text{C}_6\text{H}_5$ ),



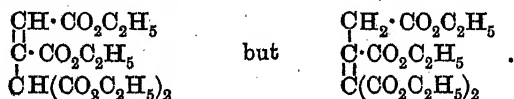
and



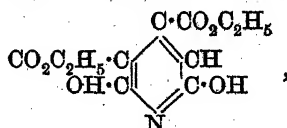
which thus have to be considered, preference had been given to the second, since ammonia does not act on these additive compounds with formation of pyridine derivatives.\* On the other hand, the behaviour of *o*-phenylenediamine towards ethyl acetylenedicarboxylate points to the first formula, as we find that the diamine reacts with this salt, forming *ethyl quinocaxidoneacetate*, according to the equation



This result would correspond to the view expressed in formula I regarding the constitution of the products formed by the union of ethyl acetoacetate and ethyl benzoylacetate with ethyl acetylenedicarboxylate. Moreover, this formula is supported by the following considerations. It may be assumed that ethyl malonate would resemble the ester of the  $\beta$ -ketonic acids in its reaction with ethyl acetylenedicarboxylate. If symbol II were assigned to the former additive products, the conclusion may be drawn that ethyl malonate would also yield a trimethylene derivative with ethyl acetylenedicarboxylate. Michael (*J. pr. Chem.*, 1894, [ii], 49, 20), however, has shown that the additive compound is the ester of an unsaturated acid, since, on hydrolysis, it yields aconitic acid. These facts, whilst indicating that the substances formed by the union of the esters of  $\beta$ -ketonic acids with ethyl acetylenedicarboxylate are to be represented by formula I, would at the same time lead to the assumption that the constitution of the additive product of ethyl malonate with ethyl acetylenedicarboxylate is not



The latter formula would not be at variance with the formation of aconitic acid from the substance which it represents. It further agrees with the result of the action of ammonia on the ethyl ester of the tetracarboxylic acid. As shown below, there is thus formed *ethyl 2:6-dihydroxypyridine-3:4-dicarboxylate*,



\* As will be shown in a later communication, these esters are identical with those obtained by the action of ethyl chlorofumarate on the sodium derivatives of ethyl acetoacetate and ethyl benzoylacetate (*Trans.*, 1896, 69, 580, 1888; 1897, 71, 323).

which, on hydrolysis with hydrochloric acid, loses carbon dioxide and yields citrazinic acid.

### EXPERIMENTAL.

#### *Action of Benzamidine on Ethyl Phenylpropiolate.*

As mentioned in the previous paper (Ruhemann and Cunningham, *loc. cit.*), benzamidine hydrochloride and ethyl phenylpropiolate react in the presence of sodium ethoxide to form benzalphenylglyoxalidone. We now find that for the preparation of this compound 1 mol. of the ethoxide is sufficient, but that the reaction takes a different course, if, instead of allowing the mixture to stand at the ordinary temperature, it is heated on the water-bath for 2—3 hours. On adding water and a little acetic acid to the contents of the flask, a yellow solid is precipitated which dissolves in boiling glacial acetic acid, and, on cooling, crystallises out in yellowish needles melting at  $284^{\circ}$ , whilst the melting point of benzalphenylglyoxalidone is  $274^{\circ}$ .

The percentage composition of this substance, as ascertained by the following analysis, is, however, identical with that of the compound of lower melting point.

0.2010 gave 0.5695  $\text{CO}_2$  and 0.0910  $\text{H}_2\text{O}$ .  $\text{C} = 77.15$ ;  $\text{H} = 5.02$ .

0.2871 „ 28 c.c. moist nitrogen at  $23^{\circ}$  and 767 mm.  $\text{N} = 11.08$ .

$\text{C}_{16}\text{H}_{12}\text{ON}_2$  requires  $\text{C} = 77.41$ ;  $\text{H} = 4.83$ ;  $\text{N} = 11.29$  per cent.

The two compounds differ, not only in their melting points, but also in their other properties. Whilst benzalphenylglyoxalidone, when treated with concentrated hydrochloric acid, at first dissolves although the solution immediately sets to a solid, the second substance, which is also soluble in the concentrated acid, remains in solution. This fact, as well as the readiness with which the latter dissolves in caustic potash, agrees with the statements of the behaviour of *diphenylpyrimidone*. The compound differs from the pyrimidone as it has a yellow colour and evolves benzaldehyde when boiled with caustic potash. A closer examination has shown, however, that these properties are due to benzalphenylglyoxalidone contained in the above product, as the solution of the latter in concentrated hydrochloric acid, on standing for a day, gives a separation which, after crystallisation from glacial acetic acid, melts at  $274^{\circ}$  and has all the properties of this compound. The presence of diphenylpyrimidone in the substance melting at  $284^{\circ}$  is established by its behaviour towards bromine. On adding the halogen to a solution of the product in concentrated hydrochloric acid, a white precipitate is at once formed which crystallises from glacial acetic acid in colourless needles melting at  $297$ — $298^{\circ}$ , and has the composition  $\text{C}_{16}\text{H}_{11}\text{ON}_2\text{Br}$ .



0.2498 gave 0.1420 AgBr. Br = 24.20.

0.2310 „ 16.8 c.c. moist nitrogen at 16° and 765 mm. N = 8.53.

$C_{16}H_{11}ON_2Br$  requires Br = 24.46; N = 8.56 per cent.

Diphenylpyrimidone, which we have prepared according to Pinner's directions (see "Die Imidoäther und ihre Derivate," 1892, p. 254; we find the melting point to be 287—288°, compared with 284° as found by Pinner), yields, under similar conditions, a bromo-derivative which in every respect is identical with our compound. Its composition,  $C_{16}H_{11}ON_2Br$ , has been verified by the following nitrogen determination:

0.2303 gave 16.5 c.c. moist nitrogen at 16° and 765 mm. N = 8.40.

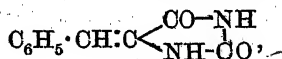
After having thus proved that benzamidine reacts with ethyl phenylpropionate at a higher temperature to form a mixture of benzalphenylglyoxalidone and diphenylpyrimidone, we were anxious to effect their complete separation. Although the solution of the mixture in concentrated hydrochloric acid deposits the glyoxalidone derivative on standing, yet a certain amount remains in the filtrate, and, on the addition of water, is precipitated along with the diphenylpyrimidone. Even on boiling the mixture with caustic potash for some hours, only partial decomposition of the glyoxalidone takes place. The product obtained on acidifying the alkaline solution and recrystallising the precipitate from glacial acetic acid still has a yellow colour, and even after prolonged boiling with alkali the odour of benzaldehyde is still perceptible. Diphenylpyrimidone can, however, be isolated from the mixture in a pure state by making use of the fact that it is very stable, whilst benzalphenylglyoxalidone, although only partially decomposed by alkalis and acids, is readily destroyed by oxidising agents. Fuming nitric acid is especially convenient for this purpose, for, as we have ascertained, it does not give rise to nitro-compounds when added to the solution of diphenylpyrimidone in glacial acetic acid, whilst the glyoxalidone is thus transformed into readily soluble substances. In order to isolate the pyrimidone from the mixed product which is formed by digesting a mixture of benzamidine and ethyl phenylpropionate on the water-bath, it is sufficient to treat its solution in glacial acetic acid with fuming nitric acid, and then to add water. By this means, a solid is precipitated which crystallises from glacial acetic acid in colourless prisms, and has all the properties characteristic of diphenylpyrimidone. Its composition has been verified by the following nitrogen determination:

0.2252 gave 22 c.c. moist nitrogen at 18° and 767 mm. N = 11.32.

$C_{16}H_{12}ON_2$  requires N = 11.29 per cent.

*Action of Urea, Thiourea, and Guanidine on Ethyl Phenylpropiolate.  
Benzalhydantoin.*

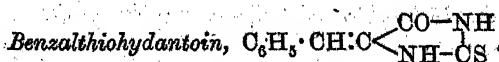
We have already mentioned in the introduction to this paper that the compound which is formed by the action of sodium ethoxide on a mixture of urea and ethyl phenylpropiolate has not the structure  $C_6H_5C:O \cdot CO \cdot NH \cdot CO \cdot NH_2$ , as has been stated previously (*loc. cit.*), but



This formula, which represents the compound as benzalhydantoin, follows from its behaviour towards alkali. Although it is freely soluble in dilute caustic potash and is precipitated unchanged by hydrochloric acid, yet a concentrated solution of the alkali only gradually dissolves it on boiling, and at the same time, decomposition takes place. At first, the odour of benzaldehyde is perceptible, and, later, an evolution of ammonia sets in, which ceases after the heating has been continued for three hours. The alkaline liquor, on being acidified with hydrochloric acid, yields a solid which readily dissolves in ether and crystallises from chloroform in colourless plates. This compound is characterised as  $\alpha$ -hydroxycinnamic acid (phenylpyruvic acid) by its melting point,  $154-155^\circ$ , the green coloration it gives with ferric chloride, and by the following analysis:

0.2206 gave 0.5339  $CO_2$  and 0.0969  $H_2O$ . C = 66.00; H = 4.88.

$C_9H_8O_3$  requires C = 65.85; H = 4.87 per cent.



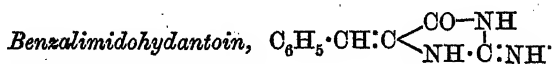
This compound is obtained in a similar manner to benzalhydantoin by mixing alcoholic solutions of sodium ethoxide and thiourea with ethyl phenylpropiolate. After standing for several hours, the alcohol is removed by evaporation, and then water and a little dilute sulphuric acid are added. A yellowish solid is precipitated, which is insoluble in water, and only sparingly soluble in alcohol or boiling glacial acetic acid. From the solution in the latter solvent, it gradually separates, on adding water, as a yellowish powder, which is washed with alcohol and dried at  $100^\circ$ . On slowly heating, it decomposes about  $280^\circ$ , but, when the temperature is rapidly raised, decomposition takes place at  $300^\circ$ . On analysis:

0.2081 gave 23.5 c.c. moist nitrogen at  $15^\circ$  and 764 mm. N = 13.30

0.2740 " 31.5 " " 17 " 764 mm. N = 13.40,

$C_{10}H_9ON_2S$  requires N = 13.72.

On boiling this compound with concentrated caustic potash for three hours in a flask fitted with a reflux condenser, it suffers a decomposition analogous to that of benzalhydantoin and yields  $\alpha$ -hydroxycinnamic acid. This is isolated by acidifying the alkaline liquor with hydrochloric acid, extracting the solution with ether, and removing the solvent by evaporation. The residue, recrystallised from chloroform, shows all the properties characteristic of  $\alpha$ -hydroxycinnamic acid.



When alcoholic solutions of sodium ethoxide, guanidine thiocyanate and ethyl phenylpropionate (1 mol. of each) are mixed a yellowish-red coloration is produced, and, on slightly warming on the water-bath, the contents of the flask set to a semi-solid mass. The product is almost insoluble in water or alcohol, but dissolves in boiling glacial acetic acid, from which, on carefully adding water, it separates in yellowish, microscopic needles. These darken at about  $285^\circ$  and melt at  $295^\circ$  to a black liquid. On analysis:

0.2030 gave 0.4785  $\text{CO}_2$  and 0.0900  $\text{H}_2\text{O}$ .  $\text{C} = 64.18$ ;  $\text{H} = 4.92$ .

0.2570 „ 47.5 c.c. moist nitrogen at  $10^\circ$  and 768 mm.  $\text{N} = 22.36$ .

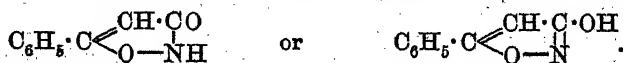
$\text{C}_{10}\text{H}_9\text{ON}_3$  requires  $\text{C} = 64.17$ ;  $\text{H} = 4.78$ ;  $\text{N} = 22.46$  per cent.

This compound possesses both acidic and basic properties. It freely dissolves in hot concentrated hydrochloric acid, and the solution, on cooling, deposits yellowish needles of the hydrochloride; this, however, is unstable, and on drying loses hydrogen chloride.

Its constitution is proved, as in the former cases, by the decomposition which the substance suffers under the influence of caustic potash; when boiled with it, the odour of benzaldehyde is developed, an evolution of ammonia takes place, and an acid is formed which we have proved to be  $\alpha$ -hydroxycinnamic acid.

*Action of Hydroxylamine on Ethyl Phenylpropionate 5-Phenyl-3-isoxazolone.*

The results of our experiments, which are described above, induced us to re-examine the product of the action of hydroxylamine on ethyl phenylpropionate. A closer study of this substance has shown that it is not a hydroxamic acid, but a cyclic compound of the formula



This constitution follows from the remarkable stability of the

substance towards acids and alkalis. Even on boiling it with these reagents for some hours, hardly any decomposition takes place, although a substance of the formula  $C_6H_5 \cdot C \equiv C \cdot C(N \cdot OH) \cdot OH$ , might be expected to readily break up into phenylpropionic acid and hydroxylamine.

To the description of the properties of the isoxazolone contained in the previous paper, we add the following cryoscopic determination of the molecular weight, glacial acetic acid being used as the solvent.

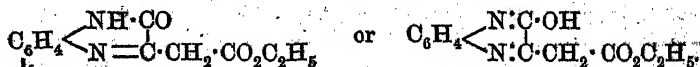
Weight of substance.	Weight of solvent.	Depression.	Mol. wt.
0.625	21.62	0.73°	161.

$C_9H_7O_2N$  requires mol. wt. = 169

Further experiments, which we intend to perform, are necessary in order to ascertain whether in the methyl derivative,  $C_9H_6O_2N \cdot CH_3$ , the alkyl group is united with the nitrogen or with the ketonic oxygen of the isoxazolone.

*Action of o-Phenylenediamine on Ethyl Acetylenedicarboxylate.*

We have pointed out already that ethyl acetylenedicarboxylate and ethyl phenylpropiolate seem to show differences in their behaviour with organic bases similar to those with esters of  $\beta$ -ketonic acids. Of special interest in this respect is the fact that ethyl phenylpropiolate does not condense with o-phenylenediamine whilst ethyl acetylenedicarboxylate, on treatment with the base, yields a compound which is to be regarded as *ethyl quinoxalidoneacetate*.



The formation of this substance takes place on mixing an alcoholic solution of sodium ethoxide (2 mols.) with o-phenylenediamine hydrochloride (1 mol.) and ethyl acetylenedicarboxylate (1 mol.), and heating the mixture on the water-bath for 2—3 hours. After removing the alcohol by evaporation, water and a little hydrochloric acid are added, and the resulting yellow solid is washed with dilute spirit. It dissolves in boiling alcohol with great difficulty, and, on cooling, crystallises in yellow needles, which soften at 205° and melt at 210° to a red liquid.

On analysis, the following numbers were obtained:

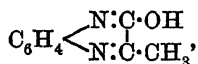
0.2074 gave 0.4714  $\text{CO}_2$  and 0.0968  $\text{H}_2\text{O}$ .  $C = 61.98$ ;  $H = 5.18$ .

0.2713 " 28.5 c.c. moist nitrogen at 17° and 763 mm.  $N = 12.23$ .

$C_{12}H_{12}O_2N_2$  requires  $C = 62.04$ ;  $H = 5.17$ ;  $N = 12.06$  per cent.

The ethyl ester has both basic and acidic properties. It dissolves

in concentrated hydrochloric acid, but the hydrochloride thus formed is decomposed by water. Whilst the solution of ethyl quinoxalidone-acetate in hydrochloric acid is yellow, its solution in dilute caustic potash is colourless; the compound, therefore, has properties characteristic of the hydroxyquinoxalines. On boiling the ester with concentrated caustic potash for 3 hours and then acidifying the alkaline liquor, carbon dioxide is evolved and a solid is precipitated. This crystallises from boiling water in almost colourless needles melting at  $245^{\circ}$ , and was found to be identical with hydroxymethylquinoxaline,



previously prepared by Hinsberg (*Annalen*, 1896, 292, 249). The composition of the substance was verified by the following analyses:

0.2184 gave 0.5395  $\text{CO}_2$  and 0.0985  $\text{H}_2\text{O}$ . C = 67.37; H = 5.01.

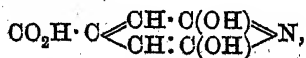
0.2303 „ 34.4 c.c. moist nitrogen at  $15^{\circ}$  and 759 mm. N = 17.47.

$\text{C}_9\text{H}_8\text{ON}_2$  requires C = 67.50; H = 5.00; N = 17.50 per cent.

*Formation of Ethyl 2:6-Dihydroxypyridine-3:4-dicarboxylate.*

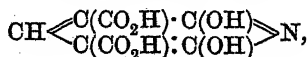
The considerations brought forward in the introduction to this paper point to the formula  $\text{CO}_2\text{C}_2\text{H}_5 \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{C}_2\text{H}_5) : \text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$  for ethyl propenetetracarboxylate, the product which Michael (*loc. cit.*; see also Ruhemann and Cunningham, *Trans.*, 1899, 75, 954) obtained by the addition of ethyl malonate to ethyl acetylenedicarboxylate. We have subjected this compound to the action of ammonia with the view of preparing ethyl 2:6-dihydroxypyridine-3:4-dicarboxylate, and thus completing the series of mono- and di-carboxylic acids of 2:6-dihydroxypyridine.

From 2:6-dihydroxypyridine, two mono- and two di-carboxylic acids can be derived. The monocarboxylic acid containing the  $\text{CO}_2\text{H}$  group in the 4-position, namely,



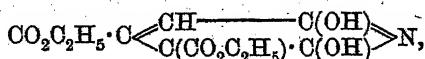
is citrazinic acid, which was discovered by Behrmann and Hofmann (*Ber.*, 1884, 17, 2687), and subsequently obtained by one of us (Ruhemann, *Ber.*, 1887, 20, 3367) in the course of his researches on the action of ammonia on the ethyl esters of unsaturated acids. The ethyl ester of the second or 3-monocarboxylic acid has lately been isolated by Errera (*Ber.*, 1898, 31, 1245).

Of the dicarboxylic acids, only ethyl dihydroxynicotinate,



has, up to the present, been recorded (see Guthzeit, *Ber.*, 1893, 26, 2795; Ruhemann and Sedgwick, *Ber.*, 1895, 28, 825; Errera, *Gazzetta*, 1897, 27, ii, 393; Ruhemann and Browning, *Trans.*, 1898, 73, 280). On hydrolysis with hydrochloric acid, it loses two mols. of carbon dioxide, and yields 2:6-dihydroxypyridine (Ruhemann, *Trans.*, 1898, 73, 350; see also Errera, *Ber.*, 1898, 31, 1246).

We find that the ethyl ester of the remaining dicarboxylic acid,



is readily prepared by placing concentrated aqueous ammonia with ethyl propenetetracarboxylate in a bottle, and agitating the mixture from time to time. In the course of 4—5 days, the oil disappears and the vessel contains a reddish solution, together with a yellowish solid. The latter we have not examined, since its amount is very small. The filtrate is concentrated by heating under diminished pressure on the water-bath, and then acidified with hydrochloric acid. This precipitates a solid, which dissolves readily in hot alcohol, but is only sparingly soluble in boiling water, and separates from the hot aqueous solution in colourless prisms, melting at 161—162°. Ferric chloride gives a reddish-violet coloration with aqueous or alcoholic solutions of the substance. On analysis:

0.2100 gave 0.3975  $\text{CO}_2$  and 0.0993  $\text{H}_2\text{O}$ . C=51.62; H=5.25.

0.2340 „ 11.5 c.c. moist nitrogen at 14° and 745 mm. N=5.66.

$\text{C}_{11}\text{H}_{13}\text{O}_6\text{N}$  requires C=51.76; H=5.10; N=5.49 per cent.

Ethyl 2:6-dihydroxypyridine-3:4-dicarboxylate, besides acidic properties, has also those of a base, since it dissolves in concentrated hydrochloric acid with the greatest ease. On boiling this solution for 3 hours, hydrolysis takes place, accompanied by the removal of 1 mol. of carbon dioxide, and there is formed a monocarboxylic acid, which is precipitated by adding water to the acid solution. This acid has been identified as citrazinic acid by direct comparison of its properties and by the following analyses:

0.1465 gave 0.2485  $\text{CO}_2$  and 0.0405  $\text{H}_2\text{O}$ . C=46.26; H=3.03.

0.2480 „ 18.5 c.c. moist nitrogen at 9° and 769 mm. N=9.08.

$\text{C}_6\text{H}_5\text{O}_4\text{N}$  requires C=46.45; H=3.22; N=9.03 per cent.

The decomposition which ethyl 2:6-dihydroxypyridine-3:4-dicarboxylate suffers on heating with hydrochloric acid is in accordance with the behaviour of the corresponding ester of the 3:5-substituted dicarboxylic acid which, as mentioned before, under the influence of boiling hydrochloric acid, loses 2 mols. of carbon dioxide. These facts show that 2:6-dihydroxypyridinecarboxylic acids with  $\text{CO}_2\text{H}$  groups

in the 3-position readily lose them with elimination of carbon dioxide.

In conclusion, it may be stated that further experiments on the lines indicated in this paper are in progress.

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CAMBRIDGE.

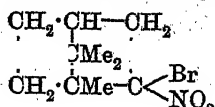
## XXV.—*Studies in the Camphane Series. Part I. Nitro-camphane.*

By MARTIN ONSLOW FORSTER.

IN a recent account of the effect produced on camphoroxime by the action of potassium hypobromite (Trans., 1899, 75, 1141), I gave a brief description of the resulting compound, which has the empirical formula  $C_{10}H_{16}O_2NBr$ . At the time of its discovery, the compound itself was not submitted to close examination, because the chief interest attaching to it lay in the fact that, by a series of apparently simple changes, it may be transformed into isolauronic acid,  $C_9H_{14}O_2$ .

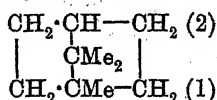
The action of potassium hypobromite on oximes has not been studied systematically, but Piloty has shown that bromine converts acetoxime into bromonitrosopropane (*Ber.*, 1898, 31, 452), and when camphoroxime is oxidised with potassium ferricyanide or permanganate, a nitroso-compound is produced. These considerations, coupled with the result of applying Liebermann's test, led to the belief that the compound  $C_{10}H_{16}O_2NBr$  is a bromonitroso-derivative, but it was pointed out that the oxidation of camphoroxime with potassium hypobromite not only involves removal of hydrogen, as in the conversion of acetoxime into bromonitrosopropane, but results also in addition of oxygen, so that the apparent analogy between the two changes is not complete.

In the present paper, evidence is brought forward to show that the product of the action of potassium hypobromite on camphoroxime is a nitro-compound, in spite of the fact that it gives Liebermann's reaction for nitroso-derivatives, and assuming Bredt's structural representation of camphor to be correct, there is every reason to believe that the substance has the constitution expressed by the formula



If the saturated hydrocarbon,  $C_{10}H_{18}$ , of which camphor is a ketonic derivative, is spoken of as *camphane*, the above compound must be

called *bromonitrocamphane*, and it becomes necessary to adopt a prefix which will show that both substituents are attached to the same carbon atom. Considering that the actual arrangement of the carbon atoms in the camphor molecule is still under discussion, it would be premature to indicate each one by a number, on the principle adopted for derivatives of benzene or naphthalene, but as the existence of the group  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  in camphor is universally admitted, there can be little objection to using the first two numerals in the formula for camphane as represented by the scheme



This order appears more suitable than the converse because in the future, when the constitution of camphor has been finally decided and the orientation of camphane derivatives requires elaboration, the carbon atom of the methylene group which corresponds to the carbonyl radicle in camphor will become a natural starting point in any system of numbering which may be ultimately adopted. The use of these numerals will obviate confusion with derivatives of camphor, which are distinguished by letters of the Greek alphabet; at the same time, it leaves room for differentiating the possible stereoisomerides of a disubstituted camphane in which the substituents are attached to the same carbon atom.

According to this nomenclature, borneol and bornylamine would be referred to as *1-hydroxycamphane* and *1-aminocamphane* respectively, and the product of the action of potassium hypobromite on camphor-oxime is now called *1:1-bromonitrocamphane*.

When bromonitrocamphane is heated with alcoholic potash, bromine is replaced by hydrogen, and *1-nitrocamphane* is produced. From the formula of this compound,  $\text{C}_8\text{H}_{14}\begin{array}{c} \text{CH}_3 \\ < \\ \text{CH}\cdot\text{NO}_2 \end{array}$ , it will be recognised that, as a secondary nitro-derivative, it should resemble phenylnitromethane in its property of occurring in two modifications. This resemblance has been found to exist, nitrocamphane being obtainable in two solid forms, one of which, representing the normal modification, is stable, melts at  $147\text{--}148^\circ$ , and has  $[\alpha]_D + 4.6^\circ$ , whilst the pseudo-modification, which rapidly changes spontaneously into the normal form, melts at  $74^\circ$ , and has  $[\alpha]_D - 95^\circ$  (approximately). The relation between these two substances corresponds in nearly every respect with that subsisting between the two modifications of phenylnitromethane (Hantzsch and Schultze, *Ber.*, 1896, 29, 699, 2251), which has been further illustrated by the study of similar nitro-compounds (compare Konowaloff, *Ber.*, 1896, 29, 2193; Lowry, *Trans.*, 1898, 73, 986;



1899, 75, 211). The normal isomeride, for instance, is indifferent towards alcoholic ferric chloride, which instantly develops a deep cherry-red coloration with the labile modification; the latter also combines with phenylcarbimide and alcoholic copper acetate, both of which are without action on the stable form. Normal nitrocampane is not attacked by aqueous sodium carbonate, but dissolves in caustic potash, forming the potassium derivative of the pseudo-modification; the latter isomeride dissolves readily in sodium carbonate, without liberating carbon dioxide, and this gas reprecipitates it from solutions in alkalis.

From the formulæ,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NO}_2 \\ \diagup \text{CO} \end{smallmatrix}$  and  $C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \text{CH} \cdot \text{NO}_2 \end{smallmatrix}$ , which represent  $\alpha$ -nitrocamphor and 1-nitrocampane respectively, it is clear that the substances are closely related; in spite of general similarity in properties, however, they differ from one another in an important characteristic. Solutions of normal nitrocampane in alcohol or benzene do not exhibit mutarotation, and hitherto the conversion into pseudonitrocampane has been effected only by the agency of concentrated aqueous potash; the labile modification, liberated from solutions in alkali by addition of acid, changes spontaneously when solid or dissolved, and becomes almost completely transformed into the normal modification. Normal nitrocamphor, on the other hand, changes into the pseudo-form when dissolved in organic solvents, but the transformation affects only about 7 per cent. of the material, when a condition of equilibrium is reached (Lowry, Trans., 1899, 75, 216).

It is noteworthy that the conversion of pseudonitrocampane into the stable modification is greatly accelerated by the action of light. The diminution in specific rotatory power which is displayed by an alcoholic solution preserved in darkness during three hours, was found to be only two-thirds of that undergone by a portion of the same liquid when exposed to light during the same interval of time; in other words, the period required by a solution of pseudonitrocampane to reach a given degree of specific rotatory power is about twice as long when the liquid is protected from light as it is when the substance is exposed to this influence. Piperidine and alkalis also exert an accelerating effect on the transformation of the labile compound.

In the present paper, I have represented pseudonitrocampane by the formula  $C_{10}H_{16} \cdot N(OH) \cdot O$ , this expression being of the type  $R \cdot CH \cdot N(OH) \cdot O$ , proposed for pseudonitro-compounds by Nef. It is unnecessary to discuss the general question of the advantages which this type offers over that represented by the formula  $R \cdot CH \begin{smallmatrix} \text{N} \cdot \text{OH} \\ \diagup \text{O} \end{smallmatrix}$ , originally suggested by Hantzsch, because the last-named investigator now

employs Nef's formula (*Ber.*, 1899, 32, 575). But its application in the case of pseudonitrocamphane may appear to require some justification because the closely allied substance, pseudonitrocamphor, has been

recently represented by the alternative formula,  $C_8H_{14} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{CO} \quad \text{N} \cdot \text{OH} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \quad \text{O} \end{array}$

(Lowry, *Trans.*, 1899, 75, 212). Two reasons for this course are given by Lowry (*Trans.*, 1898, 73, 995) in the following terms, "first, the extremely high rotatory power of the substance is most readily

explained by a formula such as  $C_8H_{14} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{CO} \quad \text{N} \cdot \text{OH} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \quad \text{O} \end{array}$ , in which the  $\alpha$ -carbon atom is asymmetric, rather than by a formula in which this

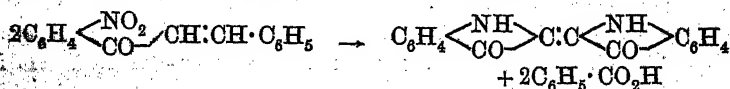
asymmetry does not occur, as in  $C_8H_{14} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{CO} \quad \text{N} \cdot \text{O} \cdot \text{OH} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \quad \text{O} \end{array}$ . Secondly, the

decomposition of the anhydride of pseudonitrocamphor by heat into camphorquinone and nitrous oxide cannot be explained in any simple way except by the use of a formula such as that already given for the substance, in which one oxygen atom is shown to be attached to the  $\alpha$ -carbon atom." These arguments, however, are not convincing. In the first place, the high rotatory power of the substance is explained quite as readily by the existence of the unsaturated linking in the

expression  $C_8H_{14} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{CO} \quad \text{N}(\text{OH}) \cdot \text{O} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \quad \text{O} \end{array}$ , as by the asymmetric carbon atom in the alternative formula, because Haller and Muller have shown that

compounds of the type  $C_8H_{14} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{CO} \quad \text{CHR} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \quad \text{O} \end{array}$  have a specific rotatory power which, in some cases, is ten times greater than that of camphor (*Compt. rend.*, 1899, 128, 1370; compare also Forster, *Trans.*, 1899, 75, 1149). In the second place, direct attachment of oxygen to the  $\alpha$ -carbon atom cannot be claimed in the case of chloronitrocamphor,

$C_8H_{14} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{CO} \quad \text{Cl} \cdot \text{NO}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \quad \text{O} \end{array}$ , yet this substance, like the anhydride of pseudonitrocamphor, yields camphorquinone when heated; these are probably examples of intramolecular oxidation, of which several instances are known, notably the action of sunlight on benzylidene-*o*-nitroacetophenone, which yields indigo and benzoic acid,



(Engler and Dorant, *Ber.*, 1895, 28, 2497). As evidence of the unsaturated character of pseudonitrocamphane, it may be mentioned that in chloroform solution it decolorises bromine instantaneously, and

the same effect is produced by a solution of the benzoyl derivative, whilst an ice cold solution of the potassium derivative is oxidised by potassium permanganate.

When the normal modification of nitrocamphane is reduced in alcoholic solution with zinc dust, or, preferably, aluminium amalgam, 1-hydroxylaminocamphane is formed, which, from its origin, and the fact that bornylamine is also produced, must be represented by the

formula  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ CH \cdot NH \cdot OH \end{smallmatrix}$ . This substance would, perhaps, be more suitably named  $\beta$ -bornylhydroxylamine, in order to indicate its relation to bornylamine,  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ CH \cdot NH_2 \end{smallmatrix}$ . It exhibits to a marked extent the reducing properties of secondary hydroxylamines. Bornylhydroxylamine is the first substituted hydroxylamine derivative of this series, and completes a group of compounds analogous to nitrobenzene, phenylhydroxylamine, and aniline.

In its behaviour towards halogens, pseudonitrocamphane bears out the analogy to secondary nitro-compounds of the aliphatic series.

Chlorine converts it into 1:1-chloronitrocamphane,  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ CCl \cdot NO_2 \end{smallmatrix}$ , bromine regenerates 1:1-bromonitrocamphane, whilst iodine gives rise to 1:1-iodonitrocamphane,  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ CI \cdot NO_2 \end{smallmatrix}$ . When treated with nitrous acid, it yields an unstable, blue substance, which is probably a

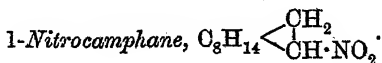
hydrate of the pseudonitrole,  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ C(NO) \cdot NO_2 \end{smallmatrix}$ . Potassium permanganate, as already stated, oxidises the alkali derivatives, and produces camphor, which is also obtained by the action of alcoholic potash on the normal modification, probably owing to initial production of the labile form.

There is no fresh evidence relating to the action which gave rise in the first instance to bromonitrocamphane, and the conversion of the oxime,  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ C \cdot N \cdot OH \end{smallmatrix}$ , into the derivative,  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ CBr \cdot NO_2 \end{smallmatrix}$ , still appears somewhat remarkable. In preparing the substance, it has been noticed invariably that the oxime is rapidly changed into a bright green compound, and the product, even when thoroughly washed, remains green until dried by exposure to air, when it becomes pale yellow. This behaviour suggests that a nitroso-derivative is first

formed, perhaps of the type  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ CBr \cdot NO \end{smallmatrix}$ ; further oxidation of such a substance might be expected to yield the hydrate,  $C_8H_{14} \begin{smallmatrix} CH_2 \\ | \\ CBr \cdot N(OH)_2 \cdot O \end{smallmatrix}$ , represented by the green product, which be-

comes pale yellow when dried. Removal of the elements of water from the hydrate would lead to bromonitrocamphane.

#### EXPERIMENTAL.



100 grams of bromonitrocamphane, prepared by oxidising camphoroxime with potassium hypobromite, were dissolved in 250 c.c. of alcohol and treated with a solution of 20 grams of caustic potash (1 mol.) in the minimum quantity of water, when a somewhat vigorous action took place. After an interval, the liquid was heated in a reflux apparatus during 8 hours, the greater part of the alcohol being then distilled off on the water-bath. Water having been added, a current of steam was passed through the liquid, and when the remainder of the alcohol had been removed, the oily distillate solidified in the tube of the condenser. Towards the end of the distillation, which was continued until all the nitrocamphane had passed over, the product was darkened by a yellow impurity, which, being an oil, greatly increases the solubility of the substance; the later fractions were therefore collected separately from those obtained at first, the total yield amounting to 55 grams.

In the earlier experiments on the reduction of bromonitrocamphane with alcoholic potash, a much larger proportion (3 mols.) of the alkali was employed. The result of this procedure was to diminish the yield by decomposing a portion of the nitrocamphane produced, whilst the remainder was converted into the potassium derivative of the pseudo-modification. Consequently, the distillate succeeding the last quantity of alcohol consisted of a viscous oil having a terpene-like odour, and containing a small proportion of nitrocamphane. The residue in the distilling flask was therefore cooled and extracted with ether, which removed a resinous, non-volatile product; the aqueous portion was then freed from ether on the water-bath, cooled to about  $0^\circ$ , and treated with dilute sulphuric acid until it was very faintly acid towards litmus. The precipitate thus formed, consisting of pseudonitrocamphane, was quickly filtered, washed, suspended in water, and heated to about  $60^\circ$ , when it fused to a greenish oil, which suddenly turned yellow on further heating; simultaneously, the somewhat nitrous odour of the pseudo-modification changed to the pungent, more camphor-like smell of the stable form, and minute crystals of the latter substance appeared on the cool neck of the flask. A current of steam was then passed through the liquid until the distillate no longer solidified in the condenser.

Nitrocamphane is thus obtained as a colourless, camphor-like substance with a pleasant odour, the vapour in steam being pungent, and

very suggestive of camphor. It is extremely soluble in ether, petroleum, chloroform, or benzene, but scarcely dissolves in water; it is most conveniently crystallised from boiling alcohol, which on cooling deposits it in colourless, fern-like aggregates. The substance cannot be powdered, because in the dry state slight pressure converts it into a compact, camphor-like mass; it melts at 147—148°. On analysis:

0.2036 gave 0.4861  $\text{CO}_2$  and 0.1669  $\text{H}_2\text{O}$ .  $\text{C} = 65.11$ ;  $\text{H} = 9.11$ .

0.1992 „ 0.4797  $\text{CO}_2$  „ 0.1648  $\text{H}_2\text{O}$ .  $\text{C} = 65.67$ ;  $\text{H} = 9.19$ .

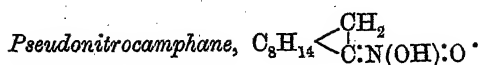
0.3514 „ 23 c.c. of nitrogen at 19° and 753 mm.  $\text{N} = 7.46$ .

$\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}$  requires  $\text{C} = 65.57$ ;  $\text{H} = 9.29$ ;  $\text{N} = 7.65$  per cent.

A solution containing 0.4992 gram of nitrocamphane in 25 c.c. of absolute alcohol at 20°, gave  $\alpha_D + 11'$  in a 2-dcm. tube, whence the specific rotatory power  $[\alpha]_D + 4.6^\circ$ ; 0.5003 gram dissolved in 25 c.c. of benzene at 20°, gave  $\alpha_D + 49'$  in the same tube, corresponding to  $[\alpha]_D + 20.4^\circ$ . The optical activity of each solution was not altered after an interval of 10 days, and was not influenced by addition of piperidine.

Nitrocamphane gives Liebermann's reaction for nitroso-compounds, and behaves like a saturated substance towards a solution of bromine in chloroform. It is insoluble in cold concentrated nitric acid, but dissolves in concentrated sulphuric acid, from which it may be precipitated by addition of water. The alcoholic solution does not develop colour with cold ferric chloride, although a slight darkening takes place on warming the liquid. Copper acetate does not give a precipitate with the solution in cold alcohol, but a small proportion of a green, gelatinous substance is produced on boiling. It is indifferent towards phenylcarbimide. The nitro-compound dissolves in hot aqueous alkalis, which convert it into the alkali derivatives of pseudonitrocamphane; alkali carbonates, however, are without action on the substance.

*Action of Alcoholic Potash.*—Twenty-five grams of nitrocamphane were dissolved in alcohol, and heated with the same weight of caustic potash in a reflux apparatus during 12 hours. The alcohol having been distilled off, a current of steam was passed through the residual liquid, which yielded 10 grams of camphor; this was identified by conversion into the oxime, which melted at 118° and gave  $[\alpha]_D - 41.0^\circ$  in a 2 per cent. solution in alcohol. The residue in the distilling flask was cooled, filtered, and acidified with dilute sulphuric acid, which precipitated a pale yellow oil; this substance gives Liebermann's reaction, and is decomposed on distillation under atmospheric pressure.



When a solution of 1-nitrocamphane in aqueous caustic potash is cooled with ice and cautiously acidified with dilute sulphuric acid, a white, flocculent precipitate is formed, differing widely from the original substance. In the first place, it dissolves very freely in cold alcohol, and the solution develops a deep cherry-red coloration with ferric chloride. It dissolves immediately in concentrated nitric acid, and if dropped into concentrated sulphuric acid is instantly decomposed, a hissing noise being produced, and much heat generated; it also unites vigorously with phenylcarbimide, and the alcoholic solution yields a pale green, gelatinous precipitate when treated with alcoholic copper acetate. These divergences from the behaviour of the original substance indicate that the white precipitate obtained on neutralising a solution of normal nitrocamphane in caustic alkalis consists of the pseudo-modification,  $C_{10}H_{16}:N(OH):O$ .

Pseudonitrocamphane is very freely soluble in organic media, and in the solid or dissolved state changes so rapidly into the stable modification that it has not been found possible to obtain it quite free from moisture. When freshly precipitated and roughly dried by means of porous earthenware, it melts at about  $74^\circ$  if the temperature is raised somewhat rapidly, but the melting point is much lower if the substance is heated slowly; it fuses to a bluish-green liquid which suddenly becomes yellow and evolves gas when further heated. The percentage of nitrogen in such a specimen was estimated, with the following result:

0.2768 gave 17.4 c.c. of nitrogen at  $17^\circ$  and 765 mm.  $N = 7.34$ .

$C_{10}H_{17}O_2N$  requires  $N = 7.65$  per cent.

In precipitating the pseudo-modification from solutions of its alkali derivatives, care must be taken to avoid adding excess of acid. When sulphuric or hydrochloric acid is added to a solution of pseudonitrocamphane in excess of alkali, the white precipitate which is formed by the first few drops redissolves on stirring the liquid; the precipitate is permanent when the solution is only faintly alkaline towards litmus, and continues to be formed until the latter is reddened. If, however, the precipitation is carried to this stage, the product is bluish-green, and after being dried is less readily powdered than if the process is interrupted before the liquid becomes acid.

The specific rotatory power of the substance is liable to considerable variation, according to the success with which the precipitation is attended. The highest value hitherto observed is  $[\alpha]_D - 94.9^\circ$  for a 1.75 per cent. solution in absolute alcohol, but doubtless the true

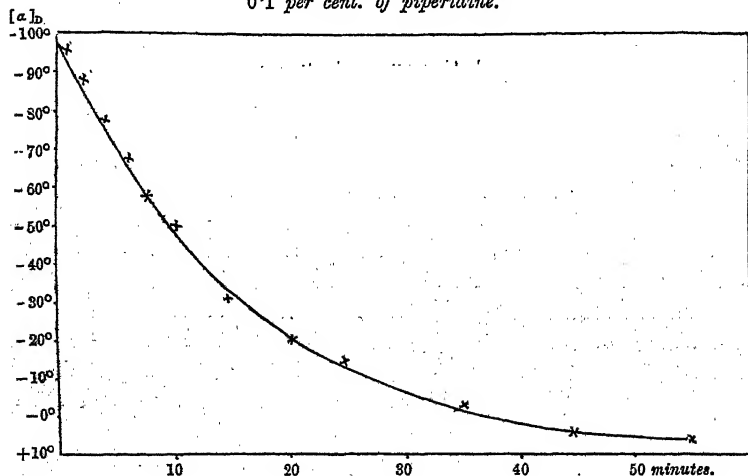
value is higher than this, because the substance has never been obtained thoroughly dry.

Specimens for examination in the polarimeter were prepared by heating normal nitrocamphane with 40 per cent. caustic potash to about  $60^{\circ}$ , and diluting considerably with water, the solution when cold being filtered and nearly acidified with dilute hydrochloric acid; the precipitate was collected, washed, and dissolved in sodium carbonate, from which, after filtration, the pseudo-modification was precipitated at  $0^{\circ}$  with ice-cold hydrochloric acid. After being dried as well as possible by means of porous earthenware, the substance was weighed and dissolved without delay, because the earlier experiments showed that the optical activity of the solution diminishes considerably with time, but although the change is rapid at first, it soon slackens, and many hours elapse before a constant value is reached. For example, the specific rotatory power of a 2.2 per cent. solution in alcohol fell  $40^{\circ}$  within 3 hours of the first observation, but a slight diminution continued to be noticeable during 10 days; even then the solution was feebly laevorotatory, indicating that conversion into the normal form was not complete. The more concentrated the solution, the more rapidly does this change take place, an alcoholic solution containing only 0.8 per cent. of the pseudo-modification having been preserved during 3 days without exhibiting a diminution in rotatory power exceeding that undergone in 3 hours by a solution of six times the concentration.

In this respect, and in its behaviour towards alkalis and piperidine, pseudonitrocamphane resembles pseudonitrocamphor. The accelerating influence of alkalis was shown by adding one drop of an aqueous solution of caustic potash to a dissolved specimen of pseudonitrocamphane giving  $[\alpha]_D - 87.6^{\circ}$ ; within 5 minutes, the specific rotatory power had fallen to  $-29^{\circ}$ , and the final reading, reached within an hour of adding the alkali, gave  $[\alpha]_D + 4^{\circ}$ . The amount of potash added was about 5 milligrams. The effect of piperidine is illustrated by the following experiment. A 1.25 per cent. solution of pseudonitrocamphane gave  $[\alpha]_D - 86^{\circ}$  within a few minutes of being prepared; one drop of an alcoholic solution of piperidine was then added, the amount of base thus introduced being the same as if the pseudonitrocamphane had been originally dissolved in a 0.1 per cent. solution of piperidine in alcohol. Within 10 minutes, the specific rotatory power was  $[\alpha]_D - 35^{\circ}$ , whilst the final value, observed within 35 minutes of adding the base, corresponded to  $[\alpha]_D + 4^{\circ}$ . The actual values recorded during a similar experiment are represented in the curve on p. 260, the form of which is typical also of those obtained on plotting the observations made during a spontaneous diminution in rotatory power.

That this change in the rotation of pseudonitrocamphane is due to the influence of piperidine, and not to the formation of piperidine salt, is shown in several ways. In the first place, the quantity present is far too small to combine with more than a small fraction of the pseudonitrocamphane in the solution; moreover, the final reading, which agrees closely with that required by the specific rotatory power of normal nitrocamphane, is scarcely altered on adding a drop of concentrated hydrochloric acid to the solution. It is probable also that a piperidine derivative of pseudonitrocamphane would be lævo-rotatory, like the potassium and benzoyl derivatives. Finally, the diminution in the intensity of the colour developed by ferric chloride is concurrent with the fall in specific rotatory power, proving that the pseudo-modification is transformed into the normal compound.

*Fall in rotation of pseudonitrocamphane dissolved in alcohol containing 0.1 per cent. of piperidine.*



In the introductory section of this paper, reference was made to the influence exerted by light on solutions of pseudonitrocamphane. A 1 per cent. solution in absolute alcohol was prepared in a darkened room and divided into two portions, one of which was exposed to direct sunlight (in January) for 3 hours; the other was examined without delay in the polarimeter, and was protected subsequently from light. At the end of the period mentioned, the specific rotatory power of the exposed solution had fallen 39°, that of the protected solution being diminished by only 24°. After an interval of 7 hours from the time the solution was prepared, the specific rotatory power of the protected portion had fallen 39°, the time occupied being therefore more than twice as long as in the case of the liquid which had



been exposed to sunlight. In another experiment, in which a solution was left in diffused daylight, followed by electric light, for a total period of 9 hours, the fall in rotatory power was equal to that exhibited by a portion of the same solution which had been preserved in darkness during 23 hours.

When pseudonitrocamphane is placed in a desiccator or exposed to air, it quickly changes from a white powder to a bluish, semi-solid mass. Before the transformation is noticeable in the appearance of the substance, it may be detected by the melting point; a specimen melting at  $71^{\circ}$ , for instance, was still powdery, and not apparently altered after an interval of 3 hours, but the melting point was then  $65^{\circ}$ . When acetyl chloride is added to an ice-cold solution of the freshly precipitated substance in ether, the liquid becomes deep yellow, then green, and finally bright blue; the solid compound is converted into a bright blue oil by cold concentrated hydrochloric acid (compare Hantzsch and Schultze, *loc. cit.*).

An ice-cold solution of pseudonitrocamphane in chloroform instantly decolorises bromine. The solution in glacial acetic acid is blue, and is too deep in colour to admit of the examination of a 2 per cent. solution in a 2 dm. polarimeter tube. The solution in benzene is colourless, but becomes blue and turbid after an interval of a few minutes.

*Potassium Derivative.*—When a solution of nitrocamphane in aqueous caustic potash is allowed to evaporate spontaneously in a desiccator, the potassium derivative of the pseudo-modification separates in white crystals. On analysis:

0.2122 gave 0.0844  $K_2SO_4$ .  $K = 17.87$ .

$C_{10}H_{16}O_2NK$  requires  $K = 17.64$  per cent.

The substance is extremely soluble in cold water, forming a solution which is alkaline towards litmus; it also dissolves freely in alcohol. A solution containing 0.2781 gram in 25 c.c. of absolute alcohol at  $18^{\circ}$  gave  $[\alpha]_D -1^{\circ}41'$  in a 2 dm. tube, whence  $[\alpha]_D -75.6^{\circ}$ , but this value is only approximate, because it was found necessary to filter the solution; the optical activity of the liquid remained constant.

*Benzoyl Derivative.*—Nitrocamphane was dissolved in considerable excess of aqueous caustic potash and agitated with benzoyl chloride, which soon gave rise to a pale green, viscous oil; this was allowed to remain in contact with dilute potash for several hours, and when quite free from benzoyl chloride was extracted with ether. After drying the ethereal solution with calcium chloride, it was evaporated in a vacuum desiccator at the temperature of the air. The dark green oil decomposed vigorously when distilled under the ordinary pressure

and being only slightly volatile in steam, it was analysed without further treatment after exposure to dry air during several days.

0.2149 gave 0.5660  $\text{CO}_2$  and 0.1510  $\text{H}_2\text{O}$ .  $\text{C} = 71.83$ ;  $\text{H} = 7.81$ .

$\text{C}_{17}\text{H}_{21}\text{O}_8\text{N}$  requires  $\text{C} = 71.08$ ;  $\text{H} = 7.32$  per cent.

The benzoyl derivative is a dark green, very viscous oil, and is almost odourless; an ice-cold solution in chloroform immediately decolorises bromine. As might be anticipated from its appearance and origin, the substance gives Liebermann's reaction for nitroso-derivatives.

A solution containing 0.4947 gram in 25 c.c. of absolute alcohol at  $21^\circ$  gave  $[\alpha]_D - 46'$  in a 2 dm. tube, whence  $[\alpha]_D - 19.3^\circ$ .

An attempt to regenerate nitrocamphane from the benzoyl derivative by the action of alcoholic potash (1 mol.) gave rise to ethyl benzoate and camphoroxime.

*Action of Nitrous Acid.*—Nitrocamphane was dissolved in aqueous potash, filtered, and mixed with excess of sodium nitrite; dilute sulphuric acid was then added to the well-stirred ice-cold solution, which yielded a bright blue precipitate. This was collected, washed, and dried on porous earthenware, but after exposure to air the substance soon lost its blue colour, and became moist and sticky. The freshly prepared compound, after being similarly dried, softened at about  $60^\circ$  and melted somewhat indefinitely at  $70^\circ$ , forming a deep blue liquid which soon evolved gas and became yellow.

It was anticipated that the substance produced in the manner described would be the pseudonitrole,  $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{C}(\text{NO}) \cdot \text{NO}_2 \end{smallmatrix}$ , but on estimating the nitrogen in a roughly dried specimen, the following result was obtained:

0.1383 gave 14.7 c.c. at  $19^\circ$  and 770 mm.  $\text{N} = 12.40$ .

$\text{C}_{10}\text{H}_{16}(\text{NO}) \cdot \text{NO}_2$  requires  $\text{N} = 13.21$  per cent.

The difference between the found and calculated percentages of nitrogen is greater than even the undried character of the specimen appears to warrant. It is probable that the substance in question is not a pseudonitrole of the ordinary type, but a hydrate of the

formula  $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{C}(\text{NO}) \cdot \text{N}(\text{OH})_2 \cdot \text{O} \end{smallmatrix}$ , derived from pseudonitrocamphane

by addition of the elements of nitrous acid. This compound, the composition of which is represented by the expression  $\text{C}_{10}\text{H}_{17} \cdot \text{NO}_2 + \text{HNO}_2$ , contains 12.17 per cent. of nitrogen, and there is evidence, apart from that derived from the analysis, appearing to favour the view that this substance is produced. If the blue compound is left in a desiccator, it becomes yellow and sticky within a few hours, and bubbles of gas

appear; after several weeks the evolution of gas ceases, and the yellow solid becomes much harder. When warmed with aqueous potassium iodide, the halogen is set free, indicating that nitrous acid is readily eliminated. Furthermore, on submitting the substance to distillation in a current of steam, gas is liberated, the aqueous distillate becomes distinctly acid towards litmus, and nitrocampthane is deposited in the tube of the condenser.

*Oxidation of Pseudonitrocampthane with Potassium Permanganate.*—A 2 per cent. solution of potassium permanganate was added to a cold dilute aqueous solution of pseudonitrocampthane in caustic potash. Camphor soon appeared in the form of a white precipitate, whilst the oxidising agent was reduced to manganate. When the latter was no longer produced, the camphor was collected, washed, and identified by conversion into the oxime, which melted at  $118^{\circ}$  and did not depress the melting point of the purified substance.



Two litres of aqueous sodium hypochlorite, containing 4 grams of available chlorine per litre, were cooled with ice and treated with a suspension of 15 grams of camphoroxime in 30 grams of caustic potash dissolved in water. A white, crystalline solid began to separate almost immediately, and after an interval of 12 hours this was washed thoroughly with water, dried by exposure to air, and recrystallised twice from a solution in boiling alcohol, which deposits it in aggregates of thin, transparent, six-sided plates. When dry and compressed, the substance forms a camphor-like mass which closely resembles the bromonitro-compound; it gives Liebermann's reaction and is volatile in steam, the vapour having an irritating, pungent odour. On analysis:

0.1658 gave 0.3335  $\text{CO}_2$  and 0.1109  $\text{H}_2\text{O}$ .  $C = 54.86$ ;  $H = 7.43$ .

0.2107 „ 12.7 c.c. of nitrogen at  $19.5^{\circ}$  and 752 mm.  $N = 6.83$ .

0.2199 „ 0.1409  $\text{AgCl}$ .  $\text{Cl} = 15.83$ .

$C_{10}H_{16}O_2NCl$  requires  $C = 55.26$ ;  $H = 7.36$ ;  $N = 6.44$ ;  $\text{Cl} = 16.32$  percent.

The substance melts at  $217^{\circ}$ , forming a colourless liquid which does not immediately decompose. It is excessively soluble in organic media, but does not dissolve in water. Chloronitrocampthane resembles the bromonitro-derivative in its behaviour towards boiling aqueous caustic soda, which does not remove the halogen.

A solution containing 0.5095 gram, dissolved in 25 c.c. of absolute alcohol at  $20^{\circ}$ , gave  $\alpha_D - 2^{\circ}10'$  in a 2 dm. tube, whence  $[\alpha]_D - 53.1^{\circ}$ ; a solution of 0.5096 gram in 25 c.c. of benzene at  $20^{\circ}$  gave  $\alpha_D - 2^{\circ}56'$

in the same tube, corresponding to the specific rotatory power  $[\alpha]_D - 71.9^\circ$ .

An alternative method of preparing 1:1-chloronitrocamphane consists in adding chlorine water to an aqueous solution of potassium pseudonitrocamphane; the clear liquid rapidly becomes turbid, and a heavy, white precipitate of the chloro-derivative is formed.



As already stated in this paper, 1:1-bromonitrocamphane results on treating camphoroxime with an alkaline solution of potassium hypobromite (2 mols.), and its properties have been briefly described in a previous communication (Trans., 1898, 75, 1144).

Consistently with the character of a secondary nitro-compound, 1-nitrocamphane yields the bromo-derivative when the solution in aqueous potash is treated with potassium hypobromite; a specimen prepared by this method gave Liebermann's reaction, melted at  $220^\circ$ , and gave  $[\alpha]_D - 53.8^\circ$  in a 2 per cent. solution in absolute alcohol.

It has been mentioned (*loc. cit.*) that when bromonitrocamphane is reduced with zinc dust and acetic acid, camphoroxime is regenerated; the following experiments indicate that if zinc dust alone be used, bromonitrocamphane will yield camphoroxime, bornylhydroxylamine, or bornylamine, according to the conditions observed.

5 grams of bromonitrocamphane were dissolved in 90 per cent. alcohol, and heated with 10 grams of zinc dust in a reflux apparatus during 1 hour. The filtered solution was evaporated on the water-bath, and the residue extracted with dilute hydrochloric acid, which was then treated with excess of caustic soda, and submitted to distillation in a current of steam. The product was a solid, white base, having a faint odour of bornylamine, and probably consisting of bornylhydroxylamine contaminated with bornylamine; it softened at about  $130^\circ$ , and melted very indefinitely between that temperature and  $145^\circ$ , but when suspended in water, it reduced a cold ammoniacal solution of silver nitrate.

In the next experiment, 30 grams of bromonitrocamphane were dissolved in dilute alcohol and heated with 60 grams of zinc dust during 3 hours; the filtered solution was treated with 15 c.c. of concentrated hydrochloric acid, and deposited crystals on evaporation. The filtrate from these acquired the odour of campholenitrile on further evaporation, showing that camphoroxime was among the products of reduction. The crystalline deposit was dissolved in water, which was then boiled till odourless, filtered, and rendered alkaline with caustic soda; a current of steam having been passed through the

liquid, a distillate of bornylamine was obtained unmixed with bornyl-hydroxylamine. The specimen of bornylamine obtained in this way melted at  $162^{\circ}$ , and gave  $[\alpha]_D +41.0^{\circ}$  in a 2 per cent. solution in absolute alcohol, showing that the proportion of neobornylamine was very small compared with that formed on reducing camphoroxime with sodium and amyl alcohol; an estimation of nitrogen gave 9.24 per cent.,  $C_{10}H_{19}N$  requiring 9.15 per cent.

On reducing bromonitrocampheane in dilute alcohol with aluminium amalgam, the chief product is camphoroxime.



An aqueous solution of the potassium derivative of pseudonitrocampheane was treated with iodine dissolved in aqueous potassium iodide; the colour of the halogen was immediately destroyed, and a pale yellow, flocculent precipitate rapidly formed and settled beneath the liquid, which was decanted as soon as the iodine solution no longer gave rise to a solid derivative. The product was thoroughly washed and dissolved in hot glacial acetic acid, which was then diluted with water; when cold, the precipitate was filtered and recrystallised from the minimum quantity of hot alcohol, which was cooled as quickly as possible and filtered without delay. On analysis:

0.1841 gave 0.2610  $CO_2$  and 0.0862  $H_2O$ .  $C=38.66$ ;  $H=5.20$ .

0.3210 „ 13.1 c.c. of nitrogen at  $19^{\circ}$  and 770 mm.  $N=4.75$ .

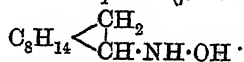
0.2124 „ 0.1608 AgI.  $I=40.91$ .

$C_{10}H_{18}O_2NI$  requires  $C=38.83$ ;  $H=5.18$ ;  $N=4.53$ ;  $I=41.10$  per cent.

Iodonitrocampheane crystallises from alcohol in pale yellow prisms which darken at about  $170^{\circ}$ , and melt at  $179^{\circ}$ , forming a deep brown liquid which rapidly undergoes further decomposition; it dissolves very readily in acetone, benzene, petroleum, or ethyl acetate, crystallising from the last named solvent in lustrous, transparent prisms. Although quite stable in the solid state, solutions in acetone and alcohol darken within a few hours, and on evaporating the solvent, a dark brown, viscous oil remains; the solution in benzene, however, may be evaporated on the water-bath without undergoing alteration.

A solution containing 0.2497 gram dissolved in 25 c.c. of absolute alcohol at  $19^{\circ}$  gave  $\alpha_D -13'$  in a 2 dm. tube, whence  $[\alpha]_D -10.8^{\circ}$ . A solution of 0.5 gram in 25 c.c. of benzene at  $20^{\circ}$  gave  $\alpha_D -36'$  in the same tube, corresponding to  $[\alpha]_D -15.0^{\circ}$ .

Iodonitrocampheane gives Liebermann's reaction for nitroso-derivatives. It slowly becomes brown on exposure to light, and is more easily decomposed than the corresponding chloro- and bromo-derivatives; for instance, hot aqueous potassium iodide withdraws iodine from the substance, and hot caustic soda also eliminates the halogen.

1-Hydroxylaminocamphane ( $\beta$ -Bornylhydroxylamine),

20 grams of aluminium (*Aluminiumgrües*) were covered with a solution of mercuric chloride in absolute alcohol prepared by diluting a saturated solution with 10 volumes of the solvent; when the action had proceeded vigorously for nearly a minute, the turbid liquid was decanted, and the amalgam washed with absolute alcohol. A solution containing 20 grams of nitrocamphane in alcohol was then poured on the amalgam, some water added, and the flask containing the material at once fitted with a reflux condenser. On warming the liquid very gently, a vigorous action took place, and was allowed to proceed during 5 minutes; at the end of this period, the contents of the flask were cooled, filtered, and treated with 20 grams of crystallised oxalic acid dissolved in the minimum quantity of hot water. Alcohol was then distilled off on the water-bath, and a current of steam passed through the liquid in order to remove non-basic bye-products; when cold, the solution was filtered and rendered faintly alkaline with caustic soda, which yielded a granular precipitate composed of the oxalates of bornylhydroxylamine and sodium. It was therefore collected, suspended in hot water, treated with excess of caustic soda, and subjected to steam distillation. The aqueous distillate, which reduced ammoniacal silver nitrate almost immediately in the cold, was then heated and employed to extract the solid portion; the filtered liquid, on cooling, deposited minute, silky needles melting at  $142^\circ$ . The solid distillate, however, after being crystallised three times from petroleum, formed transparent, oblong plates melting at  $154^\circ$ , and both forms reduced cold ammoniacal silver nitrate almost immediately. On analysis:

0.0937 gave 0.2433  $\text{CO}_2$  and 0.0949  $\text{H}_2\text{O}$ .  $\text{C} = 70.81$ ;  $\text{H} = 11.25$ .

$\text{C}_{10}\text{H}_{19}\text{ON}$  requires  $\text{C} = 71.00$ ;  $\text{H} = 11.24$  per cent.

Bornylhydroxylamine is readily soluble in hot water, and the cold solution reduces ferric chloride, ammoniacal silver nitrate, and Fehling's solution almost instantaneously; mercury acetamide is not altered by it until warmed to about  $50^\circ$ , when a grey precipitate of mercury is produced and gas evolved. It is volatile in steam, and the vapour has a very faint odour suggesting bornylamine.

A more detailed account of this substance will be given in a future communication.

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XXVI.—*The Refractive and Magnetic Rotatory Powers of some Benzenoid Hydrocarbons. The Refractive Power of Mixtures. An improved Spectrometer Scale Reader.*

By W. H. PERKIN, LL.D., Ph.D., F.R.S.

In a paper on "Magnetic Rotatory Power, especially of Aromatic Compounds," published in the Transactions of this Society, some comparisons were made between the refractive and magnetic rotatory powers of aromatic compounds (Trans., 1896, 69, 1152), but these properties were not very specially considered in relation to the benzenoid hydrocarbons, because it was thought that the numbers published up to that date for their refractive values were probably not sufficiently accurate, owing to the fact that many of the hydrocarbons had not been obtained in a pure condition. The subject, however, appeared to be worth investigation, especially on account of the irregularities found between the magnetic rotations of these substances in which methyl is substituted for hydrogen of the nucleus or the side chain, as it was of interest to see whether the refractive values were of a similar character. Having been fortunate enough to obtain specimens of many of these hydrocarbons of exceptional purity, their refractive powers were therefore determined under as nearly as possible the same conditions, using in each case the same instrument, hollow prism, &c. The magnetic rotations of the new specimens which had not already been measured were also determined.

The hydrocarbons used in this inquiry were :

Benzene,	*Cymene,
*Toluene,	* <i>o</i> -Xylene,
*Ethylbenzene,	* <i>m</i> -Xylene,
*Propylbenzene,	<i>p</i> -Xylene,
Isopropylbenzene,	Pseudocumene,
*Isobutylbenzene,	Mesitylene,
and Tetraethylbenzene.	

All those marked \* were prepared from the well-crystallised salts of the sulphonic acids, and for these I am indebted to Dr. Moody, with the exception of toluene, isobutylbenzene, and cymene, which were prepared in my own laboratory. The benzene was obtained from benzoic acid, the *p*-xylene was purified by strongly pressing the crystals between calico for a considerable time, and the isopropylbenzene was prepared from cumic acid. The pseudocumene and

mesitylene, not having yet been made from their sulphonic acids, were purified only by careful fractional distillation, and are therefore not of such well known purity as the foregoing. The tetraethylbenzene was obtained from Schuchardt, and was carefully fractionated.

The re-determination of the magnetic rotation of ethylbenzene differs but very little from that obtained previously with the same specimen, whilst with the new specimens of propyl- and isobutyl-benzenes and of *o*-xylene rather larger differences were obtained, as will be seen by the following comparisons of the molecular rotations.

	Old Nos.	New Nos.	Diff.
Ethylbenzene .....	13.442	13.467	+ 0.025
Propylbenzene .....	14.553	14.481	- 0.072
Isobutylbenzene .....	15.615	15.770	+ 0.155
<i>o</i> -Xylene .....	13.345	13.449	+ 0.104

The rotation of the new specimen of isobutylbenzene is seen to give considerably higher numbers than those previously obtained. This was expected, and the rotation now clearly indicates the existence of the iso-group which the old one did not (*ibid.*, 1082). The rotation of *o*-xylene is also a little higher than that previously given, showing a somewhat larger difference, due to position, when compared with *p*-xylene, namely, 0.639, instead of 0.535.

The rotation of tetraethylbenzene is interesting, because it shows that the four ethyl groups introduced into the nucleus give an average result which is nearly four times that found for this group in ethylbenzene, thus:

Ethylbenzene .....	13.467
Benzene.....	11.284
$C_2H_5$ disp. H.. .....	2.183
	4
„ „ .. .....	$\times 4 = 8.732$
Benzene.....	11.284
Tetraethylbenzene .....	20.016
Found .....	19.968
Diff.....	- 0.048

Of course, as mentioned above, this is an average result, because the displacements would not have quite the same influence in all positions.



# I. REFRACTIVE POWER OF BENZENOID HYDROCARBONS AND ITS COMPARISON WITH THEIR MAGNETIC ROTATORY POWER.

From the results obtained, the following relationships are found to exist between the molecular refraction of the hydrocarbons, in which there is only *one* displacement of hydrogen in the *nucleus* by a fatty group. The numbers are for the line  $H_\alpha$ .

	$\frac{\mu_\alpha - 1}{d} \cdot p$ .	Diff. for $CH_2$ .	Diff.
Benzene.....	44.087	+ 8.239	0.395
Toluene.....	52.326		
Ethylbenzene .....	60.170	+ 7.844	0.042
Propylbenzene .....	67.972	+ 7.802	
Isopropylbenzene.....	67.877	(iso - 0.105)	- 0.040
Isobutylbenzene .....	75.639	+ 7.762	

From this table, it is seen that the introduction of methyl into the nucleus gives for the change in composition by  $CH_2$  a number considerably higher than that found for subsequent additions which are not in the nucleus, but in the side chain, and that these amounts gradually diminish for each addition, although in every case they are higher than the ordinary value for  $CH_2$  in the fatty series, namely, 7.6. It is also seen that the iso-group, when introduced into the open chain, gives a lower number by 0.105 than the normal group.

The following table shows the difference of refraction due to position in the xylenes :

	$\frac{\mu_\alpha - 1}{d} \cdot p$ .	Diff. for Position.	Dispersion $H_\gamma - H_\alpha$ .
<i>p</i> -Xylene .....	60.527	0.032	3.175
<i>m</i> -Xylene .....	60.495		3.134
<i>o</i> -Xylene .....	60.375	0.120	3.115

The purity of the mesitylene and pseudocumene not being so well established as that of the xylenes, a comparison of their refractive values in relation to position, where the differences are so small, would not be useful.

As previously noticed, it is seen that *o*-xylene gives lower numbers than either the para- or meta-derivative. This is also the case with other compounds (*ibid.*, 1159), but the differences are not large and will not practically interfere with the following considerations of the methyl displacements, which are in the *nucleus only*. The first table on p. 270 shows the change, or average change, of refraction in these cases for each alteration of composition by  $CH_2$ .

	$\frac{\mu_a - 1}{d} p.$	Diff. for $\text{CH}_2$ .
Toluene.....	52.326	..... 8.239
Benzene.....	44.087	
<i>p</i> -Xylene .....	60.527	$16.440 \div 2 = 8.220$
Benzene.....	44.087	
<i>m</i> -Xylene .....	60.495	$16.408 \div 2 = 8.204$
Benzene.....	44.087	
<i>o</i> -Xylene .....	60.375	$16.288 \div 2 = 8.144$
Benzene.....	44.087	
Mesitylene .....	68.631	
Benzene.....	44.087	$24.544 \div 3 = 8.181$
Pseudocumene .....	68.592	
Benzene.....	44.087	$24.505 \div 3 = 8.168$

From these results, it is seen that whether one, two, or three displacements occur in the *nucleus*, the variation in refraction for the change of composition by  $\text{CH}_2$  is very nearly the same, and very much *higher* than when it occurs in the side chain of toluene. The same result is also seen on comparing compounds having substituted side chains with their isomerides containing methyl radicles substituted in the ring, the refractions of the latter being considerably higher.

	$\frac{\mu_a - 1}{d} p.$	
<i>p</i> -Xylene .....	60.527	} $+ 0.457 \div 2 = 0.228$
Ethylbenzene.....	60.170	
Mesitylene .....	68.631	} $+ 0.659 \div 3 = 0.219$
Propylbenzene .....	67.972	

The same thing is also seen in relation to methylisopropylbenzene, or cymene, in which there are two displacements in the nucleus, and isobutylbenzene, where there is only one, the difference being very nearly that found for the xylenes.

	$\frac{\mu_a - 1}{d} p.$	
Methylisopropylbenzene ...	76.129	} $+ 0.490 \div 2 = 0.245$
Isobutylbenzene .....	75.639	

The last example to be considered in relation to these nuclear displacements is that of tetraethylbenzene. In this case, it will be convenient, for the sake of comparison, to estimate from the refractive power of this hydrocarbon that of tetramethylbenzene, and then by subtracting the value of benzene from this to find that of the  $\text{CH}_2$  groups, thus:

Ethylbenzene .....	60.170
Toluene .....	52.326
$\text{CH}_2$ outside nucleus .....	7.844

Now by subtracting 4 times this amount from the value of tetraethylbenzene, an estimate of the methyl derivative will be obtained.

Tetraethylbenzene .....	108.097
Less $7.844 \times 4 =$ .....	31.376
Tetramethylbenzene .....	76.721
Less benzene .....	44.087
Value of $\text{CH}_3 \times 4$ .....	32.634
„ $\text{CH}_2$ .....	8.158

From this estimate it therefore appears that these *large* numbers for the change of composition by  $\text{CH}_2$  continue even to the fourth displacement, and may therefore be common to all. This is very remarkable, because it would have been expected that if any change occurred, the association of groups of relatively low refraction like  $\text{CH}_2$  with benzene, which has such a high refractive value, would decrease rather than increase the refractive power.

These results differ from those obtained for the magnetic rotations in a striking manner, as will be seen from the following comparisons.

The following table gives the rotations of the *mono*-substituted derivatives of benzene :

	Mol. rot.	Diff. for $\text{CH}_3$ .
Benzene .....	11.284	0.873
Toluene .....	12.157	
Ethylbenzene .....	13.467	1.310
Propylbenzene .....	14.481	1.014
Isopropylbenzene .....	14.633	+0.152 (iso-group)
Isobutylbenzene .....	15.770	1.137

From this, it is seen that the introduction of methyl in the nucleus, gives for the change in the composition,  $\text{CH}_2$ , a much *lower* value than that found for subsequent additions which are not in the nucleus, a result opposite to that observed in the case of the refractions.\*

Where there are multiple displacements in the *nucleus*, comparisons of the magnetic rotations are somewhat difficult to make, on account of the influence of position affecting the individual numbers to a much more considerable extent than in the case of refractions. By

\* On account of the new determinations, this table differs somewhat from that previously given (Trans., 1896, 69, 1082).

taking an average of the rotation of hydrocarbons with similar radicles in each of the possible positions, this difficulty is overcome, thus :

	Mol. rot.
<i>o</i> -Xylene .....	13·449
<i>p</i> -Xylene .....	12·810
<i>m</i> -Xylene .....	12·866
Average .....	13·042
Less benzene.....	11·284
Average for $\text{CH}_2 \times 2$ .....	1·758
$\text{CH}_2$ .....	0·879

This number, it is seen, is practically the same as that for the difference between benzene and toluene, namely is 0·873, so the average effect of the two displacements in the *nucleus* is similar to that of the first.

There are not enough examples from which to get an estimate of the effect of the three displacements, but as in tetraethylbenzene we have all positions represented, it is possible to ascertain that of four. It has already been shown that the average of the four ethyl displacements in this compound is very close to the value of ethyl occurring in ethylbenzene, and therefore the average of the methyl displacements in tetramethylbenzene should be] about the same as in toluene ; this is also seen to be the case from the following method of estimation :

Mol. rot. of tetraethylbenzene .....	19·968
Less four times the diff. between ethyl- benzene and toluene $1·301 \times 4$ .....	5·204
Mol. rot. of tetramethylbenzene .....	14·764
Less benzene .....	11·284
$\text{CH}_2 \times 4$ .....	3·480
$\text{CH}_2$ .....	0·870

This is very close to that found in the first nuclear displacement already referred to, namely, 0·873.

It is therefore seen that the change in molecular rotation, due to the displacement of hydrogen by methyl in the nucleus, is on the average considerably less than that observed when substitution occurs in the side chain, being in this respect opposite in character to the refractive values.

From the paper by Dr. Gladstone and myself (Trans., 1889, 55,

750), as also from the observations made in other papers published since then (Trans., 1894, 65, 419; 1896, 69, 1167), it is shown that there is generally a correspondence between the magnetic rotation and refractive power of compounds. It has, however, been found that this is not always the case, and that it does not hold good in reference to position and the iso-group (Trans., 1896, 69, 1160), nor, as shown in this paper, in the case of displacements of hydrogen by methyl in the benzene nucleus.

### *Experimental.*

#### *Benzene, C<sub>6</sub>H<sub>6</sub>.*

Obtained from benzoic acid. This was the same specimen as used for the magnetic rotation and density determinations already described (Trans., 1896, 69, 1191). It was redistilled from phosphoric oxide.

The refractive power was found to be as follows. Density,  $d$   $8.5^\circ/4^\circ = 0.89137$ .

Line.	$\frac{\mu - 1}{d}$ .	$\frac{\mu - 1}{d}$ .	$\frac{\mu - 1}{d}p$ .
K.....	1.49878	0.55957	43.647
Li.....	1.50309	0.56440	44.023
H <sub>a</sub> .....	1.50381	0.56521	44.087
Na.....	1.50871	0.57071	44.515
H <sub><math>\beta</math></sub> .....	1.52086	0.58434	45.578
H <sub><math>\gamma</math></sub> .....	1.53154	0.59632	46.513

Dispersion  $H_\gamma - H_a = 2.426$

#### *Toluene, C<sub>7</sub>H<sub>8</sub>.*

Prepared from pure potassium *p*-toluenesulphonate (*ibid.*), and redistilled from phosphoric oxide; it boiled at  $110.6^\circ$ .

The refractive power was found to be as follows. Density,  $d$   $8.5^\circ/4^\circ = 0.87757$ .

Line.	$\frac{\mu - 1}{d}$ .	$\frac{\mu - 1}{d}$ .	$\frac{\mu - 1}{d}p$ .	Same spec. at $10.7^\circ$ .	Diff.
K.....	1.49397	0.56288	51.785	51.806	0.021
Li.....	1.49809	0.56758	52.218	—	—
H <sub>a</sub> .....	1.49891	0.56852	52.304	52.326	0.022
Na.....	1.50349	0.57373	52.784	52.800	0.016
H <sub><math>\beta</math></sub> ....	1.51528	0.58717	54.019	54.031	0.012
H <sub><math>\gamma</math></sub> ....	1.52523	0.59850	55.062	—	—

Dispersion  $H_\gamma - H_a = 2.758$ .

These two independent determinations are seen to agree very closely.

*Ethylbenzene, C<sub>8</sub>H<sub>10</sub>.*

Prepared from ethylbenzenesulphonic acid by Dr. Moody (*ibid.*, 1192). It was redistilled from phosphoric oxide and boiled at 135.5°. Five additional determinations of the magnetic rotation of this specimen gave the following average values:

<i>t.</i>	Sp. rot.	Mol. rot.	Mol. rot. corr. to 15°.
16.7°	1.9900	13.459	13.467

The refractive power was found to be as follows. Density,  $d$  8.4°/4° = 0.87697.

Line.	$\mu_{\frac{8.4}{4}^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
K .....	1.49303	0.56220	59.593
Li .....	1.49701	0.56673	60.073
H <sub>a</sub> .....	1.49781	0.56764	63.170
N <sub>a</sub> .....	1.50206	0.57249	60.684
H <sub><math>\beta</math></sub> .....	1.51316	0.58515	62.026
H <sub><math>\gamma</math></sub> .....	1.52279	0.59613	63.190

Dispersion, H <sub>$\gamma$</sub>  - H <sub>$\alpha$</sub>  = 3.020.

*Propylbenzene, C<sub>9</sub>H<sub>12</sub>.*

Prepared from propylbenzenesulphonic acid by Dr. Moody. It was distilled from phosphoric oxide and boiled at 159° corr. Density  $d$  15°/15° = 0.86711, that of the specimen previously examined and purified only by fractional distillation was 0.8668 for the same temperature, and its boiling point 159.5° (*ibid.*, 1192).

Seven determinations of the magnetic rotation of this specimen were made, the mean being

<i>t.</i>	Sp. rot.	Mol. rot.	Mol. rot. corr. to 15°.
13.3°	1.8871	14.485	14.481

The molecular rotation of the previous specimen was 14.553 (*ibid.*, 1241).

The refractive powers of the propylbenzene from Dr. Moody and of the specimen previously examined for its magnetic rotation, and purified only by fractional distillation, were determined for comparison, the details referring to the former being given below. Density,  $d$  8.3°/4° = 0.8719.

Line.	$\frac{\mu}{d} \frac{8.3^\circ}{4^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$	Previous prep.	Diff.
K .....	1.48942	0.56133	67.359	67.357	-0.002
Li .....	1.49320	0.56566	67.879	67.877	-0.002
H <sub><math>\alpha</math></sub> .....	1.49388	0.56644	67.972	67.973	+0.001
Na .....	1.49793	0.57106	68.527	68.539	-0.012
H <sub><math>\beta</math></sub> .....	1.50850	0.58321	69.984	69.990	-0.006
H <sub><math>\gamma</math></sub> .....	1.51769	0.59375	71.250	71.242	-0.008

Dispersion,  $H_\gamma - H_\alpha = 3.278$ .

From these results, it is seen that both specimens of this hydrocarbon give practically the same numbers for the refractive power. The magnetic rotations, however, show a decided difference.

*Isopropylbenzene, C<sub>9</sub>H<sub>12</sub>.*

This was the same specimen as that used previously for the measurement of the magnetic rotation (*ibid.*, 1194); on redistillation from phosphoric oxide, its relative density,  $d_{15^\circ}$ , was raised slightly from 0.8668 to 0.86755.

The refractive power was found to be as follows. Density,  $d_{7.9^\circ/4^\circ} = 0.8727$ .

Line.	$\frac{\mu}{d} \frac{7.9^\circ}{4^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$
K .....	1.48930	0.56067	67.280
Li .....	1.49280	0.56468	67.762
H <sub><math>\alpha</math></sub> .....	1.49364	0.56564	67.877
Na .....	1.49778	0.57038	68.445
H <sub><math>\beta</math></sub> .....	1.50826	0.58239	69.887
H <sub><math>\gamma</math></sub> .....	1.51722	0.59266	71.120

Dispersion  $H_\gamma - H_\alpha = 3.243$ .

*Isobutylbenzene, C<sub>10</sub>H<sub>14</sub>.*

The specimen of this hydrocarbon examined was prepared from *p*-isobutylbenzenesulphonic acid. 150 grams of *p*-isobutylbenzene obtained from Kahlbaum were dissolved in fuming sulphuric acid, and the product, consisting chiefly of the *p*-sulphonic acid, was treated with an excess of barium carbonate. The para-salt, which is sparingly soluble in water, was obtained in leaf-like crystals, and purified by recrystallising three times. The calcium salt is very similar in appearance to the barium salt, but much more soluble in water. On analysis, the barium salt gave the following numbers which agree with those obtained by Kelbe and Pfeiffer (*Ber.*, 1886, 19, 1728):

An air dried specimen, heated to 160°, lost  $H_2O = 6.236$ , that calculated for  $1H_2O$  being 6.012 per cent. The anhydrous salt, which

rapidly absorbs water when exposed to the air, was found to contain Ba = 24.24, that calculated for  $(C_{10}H_{13}O_3S)_2Ba$  being 24.30 per cent.

*p*-Isobutylbenzenesulphonic acid, obtained by boiling this salt with the theoretical amount of dilute sulphuric acid, crystallises easily, but is very soluble in water and deliquescent. It has a rough, bitter taste, which afterwards becomes somewhat sweet. For the hydrolysis of this compound, distillation with slightly diluted sulphuric acid whilst steam was blown through the mixture was at first tried, but the yield of hydrocarbon was found to be small. The acid was therefore heated in sealed tubes with rather more than twice its weight of hydrochloric acid of sp. gr. 1.195, at a temperature of 190—200°, for 6 or 7 hours, the product being afterwards distilled with steam. This method yielded about 91 per cent. of the theoretical quantity. The oil was washed, dried over potassium carbonate, and then distilled. It commenced to boil at about 155° with evolution of some hydrogen chloride, but the temperature soon rose to 169.5°. It was then digested with sodium for some time and again distilled; most of it then came over at 169.5°, a very little afterwards passing over between this and 172°. The fraction which commenced to come over at about 155° apparently contained a small quantity of an *additive* product of the hydrocarbon with hydrogen chloride, as it burnt with a green-edged flame; after heating it with sodium, the boiling point was raised to that of the hydrocarbon.

Dr. Moody was kind enough to convert some of the barium salt, from which the acid and hydrocarbon were prepared, into the chloride and amide, and found that the amide, which melted sharply at 137°, corresponded exactly with the isobutylbenzenesulphonamide described by Kelbe and Pfeiffer.

The relative density of the isobutylbenzene obtained from the sulphonic acid was 0.87130 at 15°; this is nearly the same as that of the product previously used for the determination of the magnetic rotation, and obtained by fractionating Kahlbaum's isobutylbenzene, namely, 0.8714; the boiling point was also practically the same, 169—169.5°.

The magnetic rotation of this new specimen gave, as the average of seven determinations:

<i>t</i>	Sp. rot.	Mol. rot.	Mol. rot. corrected to 15°.
13.7°	1.8484	15.777	15.770

This number is considerably higher than that obtained with the specimen fractionated from Kahlbaum's hydrocarbon, which gave 15.615 (*ibid.*, 1241). This low number was thought to be unsatisfactory at the time, and a determination of the magnetic rotation of the



new preparation was therefore desirable (*ibid.*, 1082); the higher result is about that which might be expected, and clearly shows the influence of the iso-group in this compound.

The refractive power of this specimen, and also of that of the specimen previously examined, were determined for comparison, the details of the former being only given. Density,  $d_{7.9^\circ/4^\circ} = 0.87620$ .

Line	$\mu_{\frac{7.9^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$	Fractionated specimen.	Diff.
K .....	1.49022	0.55949	74.971	74.971	—
Li .....	1.49384	0.56361	75.524	75.525	0.001
H <sub><math>\alpha</math></sub> .....	1.49459	0.56447	75.639	75.632	-0.007
Na .....	1.49851	0.56894	76.238	76.230	-0.008
H <sub><math>\beta</math></sub> .....	1.50858	0.58044	77.779	77.801	+0.022
H <sub><math>\gamma</math></sub> .....	1.51722	0.59030	79.099	79.123	+0.024

$$\text{Dispersion } H_\gamma - H_\alpha = 3.460.$$

These results show that the refraction does not indicate the difference of purity of the two samples to the same extent as the magnetic rotation, the numbers being nearly identical.

#### *o*-Xylene, C<sub>8</sub>H<sub>10</sub>.

Prepared from the pure sulphonic acid by Dr. Moody, and re-distilled from phosphoric oxide. Boiling point 144.5° (corr.). This is a higher boiling point than that of the hydrocarbon previously examined as to its magnetic rotation and purified by fractional distillation only, namely, 142.1—143.1° (*ibid.*, 1192). Its density at 15°/15° was 0.88514, which is also higher by 0.0033. It was therefore thought desirable to determine its magnetic rotation, which was as follows, the numbers being the average of six determinations:

$t$	Sp. rot.	Mol. rot.	Mol. rot. corrected to 15°.
13.6°	2.0255	13.456	13.449

The fractionated specimen previously examined gave 13.345; the new results being higher, when compared with those obtained with the para-compound (*ibid.*, 1241), show that the difference for the ortho-position is rather more pronounced than previously indicated, thus:

Mol. rot. of <i>o</i> -xylene.....	13.449
„ „ <i>p</i> -xylene.....	12.810

0.639

This difference is similar to that between pseudocumene and mesitylene, namely, 0.632 (*ibid.*, 1130).

The refractive power of this new specimen of *o*-xylene was found to be as follows. Density,  $d_{8.5^\circ/4^\circ} = 0.8899$ .

Line.	$\mu_{\frac{8.5^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$	Specimen examined by Gladstone.
K .....	1.50189	0.56399	59.783	59.80
Li .....	1.50603	0.56864	60.276	
H <sub>a</sub> .....	1.50687	0.56958	60.375	
Na .....	1.51136	0.57462	60.910	
H <sub><math>\beta</math></sub> .....	1.52291	0.58760	62.285	
H <sub><math>\gamma</math></sub> .....	1.53301	0.59896	63.490	

Dispersion  $H_\gamma - H_a = 3.115$ .

As in the case of isobutylbenzene, the more highly purified specimen, in comparison with the fractionated product, shows a distinct difference in magnetic rotation, but practically no difference in refractive power.

*p-Xylene*,  $C_8H_{10}$ .

The specimen used in the following measurements was the same as that previously described (*ibid.*, 1193), being the crystallised hydrocarbon purified by strong pressure between calico for some considerable time. It boiled at  $138.5^\circ$  (corr.), and fused at  $13.4^\circ$ .

The refractive power was found to be as follows. Density,  $d_{14.4^\circ/4^\circ} = 0.86619$ .

Line.	$\mu_{\frac{14.4^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
K .....	1.48979	0.56545	59.937
Li .....	1.49385	0.57014	60.435
H <sub>a</sub> .....	1.49462	0.57103	60.527
Na .....	1.49911	0.57621	61.078
H <sub><math>\beta</math></sub> .....	1.51050	0.58936	62.472
H <sub><math>\gamma</math></sub> .....	1.52055	0.60097	63.702

Dispersion  $H_\gamma - H_a = 3.175$ .

*m-Xylene*,  $C_8H_{10}$ .

This was prepared from the pure 4-sulphonic acid, and redistilled from phosphoric oxide before use. Boiling point  $139.3^\circ$  (*ibid.*, 1193).

The average of two sets of measurements of the refractive power is given. Density,  $d_{8.4^\circ/4^\circ} = 0.87397$ .

Line.	$\mu_{\frac{8.4^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
K .....	1.49403	0.56526	59.917
Li .....	1.49797	0.56978	60.397
H <sub>a</sub> .....	1.49878	0.57070	60.495
Na .....	1.50324	0.57581	61.035
H <sub><math>\beta</math></sub> .....	1.51469	0.58890	62.423
H <sub><math>\gamma</math></sub> .....	1.52462	0.60027	63.629

Dispersion,  $H_\gamma - H_a = 3.134$ .

A second set of measurements were also made at  $14^\circ$ , so as to compare more accurately with the numbers obtained with *p*-xylene, which as it was solid below  $13.4^\circ$ , could not be examined at a lower temperature. It is not necessary, however, to give the details as the measurements were very close to the above, the average lowering from the rise of temperature, however, amounts to 0.017 for the difference of  $5.6^\circ$ , or 0.003 for  $1^\circ$ . In the determination of the temperature difference for toluene (Trans., 1892, 61, 308) the variation was 0.0035 for  $1^\circ$ , or nearly the same amount. The molecular refraction for  $H_a$  at  $14^\circ$  will therefore be 60.478, that actually found being 60.487.

1:4-Methylisopropylbenzene (*Cymene*),  $C_{10}H_{14}$ .

This specimen was prepared from the sulphonic acid (*ibid.*, 1194). Density,  $d_{7.9/4^\circ} = 0.86700$ .

A second set of determinations was also made on a different occasion at  $7^\circ$ , and the molecular refraction obtained is given for comparison.

Line.	$\mu_{\frac{7.9^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$	Det. at $7^\circ$ .	Diff.
K .....	1.48815	0.56303	75.446	75.485	+0.039
Li .....	1.49183	0.56727	76.015	76.031	+0.016
$H_a$ .....	1.49257	0.56813	76.129	76.129	—
Na .....	1.49664	0.57282	76.758	76.777	+0.019
$H_\beta$ ....	1.50698	0.58476	78.357	78.362	+0.005
$H_\gamma$ ....	1.51599	0.59514	79.749	79.743	-0.004

Dispersion  $H_\gamma - H_a = 3.620$  at  $7.9^\circ$ , and 3.614 at  $7^\circ$ .

1:3:4-Triethylbenzene (*Pseudocumene*),  $C_9H_{12}$ .

The product described in the previous paper (*ibid.*, 1193) was used, after redistillation from phosphoric oxide; it was not prepared from a sulphonic acid.

The refractive power was found to be as follows. Density,  $d_{8^\circ/4^\circ} = 0.88567$ .

Line.	$\mu_{\frac{8^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$
$H_a$ .....	1.50625	0.57160	68.592
$H_\beta$ .....	1.52197	0.58935	70.722
$H_\gamma$ .....	1.53192	0.60058	72.070

Dispersion,  $H_\gamma - H_a = 3.478$ .

1:3:5-Trimethylbenzene (*Mesitylene*)  $C_9H_{12}$ .

This was the same specimen as that described in the previous paper (*ibid.*, 1193); it was not prepared from a sulphonic acid.

The refractive power was found to be as follows. Density,  $d_{7.6^\circ/4^\circ} = 0.87397$ .

Line.	$\mu_{\frac{7.6^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
H <sub>a</sub> .....	1.49985	0.57193	68.631
H <sub><math>\beta</math></sub> .....	1.51521	0.58950	70.740
H <sub><math>\gamma</math></sub> .....	1.52460	0.60025	72.030
Dispersion, H <sub><math>\gamma</math></sub> - H <sub>a</sub> = 3.399.			

1:2:3:4-Tetraethylbenzene, C<sub>14</sub>H<sub>22</sub>.

This hydrocarbon was obtained from Schuchardt and fractionated a few times; the specimen examined boiled at 252—254°, corr. Jacobsen gives the boiling point as 254° (*Ber.*, 1888, 21, 2818). Relative density:

$d_{4^\circ} = 0.89822$	$d_{10^\circ} = 0.89405$	$d_{15^\circ} = 0.89092$
$d_{20^\circ} = 0.88780$	$d_{25^\circ} = 0.88556$	

The average of three determinations of the magnetic rotation gave:

$t$ .	Sp. rot.	Mol. rot.
14.7°	1.6862	19.968.

The refractive power was found to be as follows. Density,  $d_{19.6^\circ/4^\circ} = 0.88664$ .

Line.	$\mu_{\frac{19.6^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
K.....	1.50017	0.56411	107.182
Li.....	1.50381	0.56823	107.963
H <sub>a</sub> .....	1.50444	0.56893	108.097
Na.....	1.50845	0.57346	108.957
H <sub><math>\beta</math></sub> .....	1.51890	0.58525	111.197
H <sub><math>\gamma</math></sub> .....	1.52798	0.59549	113.143
Dispersion H <sub><math>\gamma</math></sub> - H <sub>a</sub> = 5.046.			

## II. THE REFRACTIVE POWER OF MIXTURES.

In the paper already referred to on the "Magnetic Rotatory Power, especially of Aromatic Compounds," it is shown that the molecular rotations of a number of mixtures which were examined were lower than the rotations calculated from their constituents when the specific rotations of these were dissimilar (*Trans.*, 1896, 69, 1052). It was therefore of interest to know whether a similar difference could be traced in the refractive power of mixtures, and to ascertain whether both properties followed each other in this particular, as they do in so many other cases. The refractive power was therefore measured of some of the mixtures of which the magnetic rotation had been deter-

mined, as well as a few others which suggested themselves as likely to be of service in reference to this subject. Other experimenters have been engaged with this subject of mixtures to some extent, although not from the point of view referred to above, the latest paper being published about two years ago by Zecchini (*Gazzetta*, 1897, 27, i, 358).

The following mixtures were examined :

Heptane and ethyl nitrate.

Methylene iodide and ethyl oxalate.

Carbon disulphide and ethyl nitrate.

Benzene and heptane.

$\alpha$ -Bromonaphthalene and ethyl nitrate.

$\alpha$ -Bromonaphthalene and heptane.

Phenetole and benzyl cyanide.

The first and last were thought to be important, because in both the constituents have nearly the same refractive indices, whilst in the other cases they are more or less wide apart.

To make the results comparable, the refractive power of each of the products employed for the mixtures was also determined.

The method of calculating the results obtained with these mixtures was analogous to that used in the case of their magnetic rotations (Trans., 1896, 69, 1052), namely, treating the mixtures as chemical compounds, finding their molecular refractions, and afterwards, from the determinations of their individual constituents, calculating what this should be if no change occurred on mixing, the difference between the two sets of numbers showing the amount of change, if any, which had taken place. The densities of the mixtures being required in these calculations, the effects of the expansion or contraction which usually takes place on making them are of course taken into account. As the calculated molecular weights of the mixtures vary considerably, it was thought to be more convenient, for the purpose of comparison, to use, not the actual differences between the molecular refractions, calculated and observed, but the percentage differences they represent, especially as these are also the percentage variations between the calculated and found specific refractions.

The following results were obtained with mixtures at 15°; the experimental details from which they are taken will be found further on (p. 285, *et seq.*).

*Mixture of equal volumes of Heptane and Ethyl Nitrate.*—The composition is 1 mol.  $C_7H_{16}$  + 1.781 mols.  $EtNO_3$ . Slight expansion took place on mixing these substances. The mixture was examined as an example of two fatty compounds with very similar indices of refraction, the difference for  $H_a$  at 15° being only 0.00337.

The percentage differences between the calculated and observed values for the molecular or specific refractions were for

$$H_{\alpha} - 0.013. \quad H_{\beta} + 0.006. \quad H_{\gamma} - 0.004.$$

so that no practical variation was found in this case.

*Equal volumes of Methylene Iodide and Ethyl Oxalate.*—Composition, 1 mol.  $\text{CH}_2\text{I}_2 + 0.592$  mol.  $(\text{CO}_2\text{Et})_2$ . Originally it was intended to use ethyl nitrate instead of ethyl oxalate, but methylene iodide was found not to be miscible with this substance. On mixing the compounds, expansion occurs to a small extent.

The percentage differences between the calculated and observed values for the molecular or specific refractions were

$$H_{\alpha} - 2.09. \quad H_{\beta} - 2.42. \quad H_{\gamma} - 2.75.$$

The refractive power of this mixture is therefore very much lower than that calculated from its constituents. This is also the case in respect to the *dispersion*, as the reduction for  $H_{\gamma} - H_{\alpha}$  is  $-0.779$ .

The difference between the refractive indices of the constituents is very large, being  $0.32464$  for  $H_{\alpha}$  at  $15^{\circ}$ .

The magnetic rotation of this mixture was also once determined, but the readings were difficult to obtain as it had become slightly coloured with iodine. The molecular rotation obtained was  $19.685$ , that calculated being  $22.796$ , thus showing a great reduction, namely,  $3.111$ .

*Equal volumes of Carbon Disulphide and Ethyl Nitrate.*—Composition 1 mol.  $\text{CS}_2 + 0.733$  mol.  $\text{EtNO}_3$ . Slight expansion occurred on mixing the substances. The percentage differences between the calculated and observed values for the molecular or specific refractions were

$$H_{\alpha} - 1.08 \quad H_{\beta} - 1.33 \quad H_{\gamma} - 1.45$$

Admixture in this case also has therefore been attended with a large reduction in refractive power; there is also a considerable lowering of the molecular dispersion, amounting to  $0.278$  for  $H_{\gamma} - H_{\alpha}$ . The difference between the refractive indices of the constituents amounts to  $0.23635$  for  $H_{\alpha}$  at  $15^{\circ}$ .

The magnetic rotation of this mixture was also very considerably lower than that calculated from its constituents (*loc. cit.*, 1055).

*Equal volumes of Benzene and Heptane.*—Composition, 1 mol.  $\text{C}_6\text{H}_6 + 0.606$  mol.  $\text{C}_7\text{H}_{16}$ . Slight expansion takes place on making this mixture. The percentage differences between the calculated and observed values for the molecular or specific refractions were:

$$H_{\alpha} - 0.26 \quad H_{\beta} - 0.29 \quad H_{\gamma} - 0.29$$

The reduction in molecular dispersion amounts to  $0.029$  for  $H_{\gamma} - H_{\alpha}$ .

The falling off in this case is small, both in refraction and dispersion; the difference between the refractive indices of the constituents is, however, not very large, being 0.11140 at 15° for  $H_a$ . This result is very similar in character to that of the magnetic rotation of this mixture.

*Equal volumes of  $\alpha$ -Bromonaphthalene and Ethyl Nitrate.*—Composition, 1 mol.  $C_{10}H_7Br$  + 1.7 mols.  $EtNO_3$ . Slight expansion takes place on mixing these substances. The percentage differences between the calculated and observed values for the molecular or specific refractions were

$$H_a - 0.44 \qquad H_\beta - 0.53 \qquad H_\gamma - 0.59$$

The reduction in molecular dispersion is 0.263 for  $H_\gamma - H_a$ . The differences between the refractive indices of the constituents for  $H_a$  at 15° is considerable, amounting to 0.26614.

*Equal volumes of  $\alpha$ -Bromonaphthalene and Heptane.*—Composition, 1 mol.  $C_{10}H_7Br$  + 0.954 mol.  $C_7H_{16}$ . Slight expansion occurs on making this mixture. The percentage differences between the calculated and observed values of the molecular or specific refractions were

$$H_a - 0.24 \qquad H_\beta - 0.29 \qquad H_\gamma - 0.33$$

The reduction in molecular dispersion amounts to 0.164 for  $H_\gamma - H_a$ . The difference between the refractive indices of the constituents is also large in this case, being 0.26339 for  $H_a$  at 15°.

*Equal volumes of Phenetole and Benzyl Cyanide.*—Composition, 1 mol.  $C_8H_{10}O$  + 1.097 mols.  $C_8H_7N$ . Slight expansion also occurs when these substances are mixed. The percentage differences between the calculated and observed values for the molecular or specific refractions were

$$H_a - 0.05 \qquad H_\beta - 0.06 \qquad H_\gamma - 0.05$$

The dispersion in this case has not undergone any appreciable change. The refraction approximates very nearly to the calculated value, the refractive indices of the constituents likewise are very close to each other, the difference being only 0.01517 for  $H_a$  at 15°.

The foregoing results are quite analogous to those of the magnetic rotations of mixtures, and it is seen that when the difference between the refractive indices of the two substances of which a mixture is composed is large, the molecular refraction is considerably less than that calculated, but when it is very small, as in the cases of the first and last examples, the observed and calculated molecular refraction is nearly the same. At first sight, there is a want of consistency in the results; for example, the reductions are much smaller in the case of the mixtures containing  $\alpha$ -bromonaphthalene, although the difference between the refractive indices of the constituents are quite as large as

in the case of the mixture of carbon disulphide and ethyl nitrate. On closer consideration, however, the mixtures are found to divide themselves into two classes, those giving large and those giving small reduction; the former consist of fatty substances *only*, but the latter of *fatty* and *aromatic* compounds, as the following table shows:

Mixture of equal vols. at 15°.	Diff. between indices.	Percentage reduction for H <sub>a</sub> .
I. Heptane and ethyl oxalate ... ..	0.00337	0.015
II. Methylene iodide and ethyl oxalate ...	0.32464	2.087
III. Carbon disulphide and ethyl nitrate ...	0.23635	1.088
IV. Benzene and heptane .....	0.11140	0.264
V. $\alpha$ -Bromonaphthalene and ethyl nitrate...	0.26614	0.443
VI. $\alpha$ -Bromonaphthalene and heptane .....	0.26331	0.287
VII. Phenetole and benzyl cyanide.....	0.01517	0.050

The results obtained by Zecchini with mixtures of substances with refractive indices wide apart are in accord with the foregoing, as is seen in the case of mixtures of carbon disulphide and alcohol, of methylene iodide and carbon disulphide, and of  $\alpha$ -bromonaphthalene and alcohol, the last giving results of much the same character as the mixtures containing  $\alpha$ -bromonaphthalene described above. Cinnamaldehyde and carbon disulphide, which have very similar refractive indices, were also found, when mixed, to give numbers differing from the calculated value by only about -0.05 per cent. One mixture examined by Zecchini, namely, that consisting of cinnamaldehyde and alcohol, is unsuitable for comparison from the point of view of this paper, because of the probability of chemical union taking place between the two compounds.

With mixtures of aromatic compounds examined by Zecchini, there are two which show a reduction in refractive power where the indices differ, but not to equal extents, namely, anethole and thiocarbanil, and anethole and cinnamaldehyde, the variations being 0.065 and 0.331 per cent. respectively.

There are, however, several exceptions to the cases already referred to, thus the various mixtures examined by Zecchini of  $\alpha$ -bromonaphthalene and carbon disulphide which might have been expected to give numbers very nearly the calculated, the indices being very similar, give a slight *increase* of refractive power, amounting to about 0.113 per cent.  $\alpha$ -Bromonaphthalene, however, even with substances of very low refractive power, does not give mixtures with such a large reduction of refraction as might be anticipated judging from the behaviour of other compounds. Again, in the cases of mixtures of thiocarbanil and carbon disulphide, where the difference between the indices is again small, the results are also slightly larger than the



calculated by about 0.120 per cent. The same is also true with mixtures of anethole and carbon disulphide, where the difference between the indices is a little greater, but the number is only about 0.05 per cent. in excess of that calculated, if one rather high result is omitted. Lastly, mixtures of  $\alpha$ -bromonaphthalene and anethole, where the indices are again close, gave numbers a little above the calculated by about 0.112 per cent. The mixtures examined by Zecchini contained various proportions of the different constituents, and were not all examined at the same temperature; his results therefore are not quite comparable with those given in this paper where equal volumes at 15° were always taken and the measurements made also at 15°, but they are sufficiently analogous to give a general idea of the peculiar results obtained. It may be worth remarking here that the examination of a mixture of  $\alpha$ -bromonaphthalene and carbon disulphide in equal vols. at 15° gave results which were very similar to Zecchini's, being slightly higher than the calculated values; a slight increase in dispersion was also observed.

From all these examples of mixtures, it appears that, although the differences between the refractive indices of the components have a great deal to do with their peculiar refractive values, there also seem to be influences acting in other directions, and to get clearer views of this subject it evidently requires to be studied in a more systematic manner than has hitherto been done. Probably it would be useful to examine various series of high refracting compounds in equal volumes with *one* substance of very low refracting power, and also series of low refracting compounds mixed with *one* of very high refracting power &c., keeping the chemical as well as the physical relationships in mind. When it is remembered how greatly the molecular arrangements in fatty and aromatic compounds differ from each other, it is not surprising that, with respect to their refractive values, such substances should produce different effects in mixtures.

### *Experimental.*

#### *Mixture of equal volumes of Heptane and Ethyl Nitrate at 15°.*

Density,  $d_{15^\circ/15^\circ} = 0.89599$ , average density at 15°/15° of the two products is 0.90231, showing an expansion on mixing which influences the density by 0.00632. Composition, 1 mol.  $C_7H_{16}$  + 1.781 mols.  $EtNO_3$ . Mol. wt. 262.072. Density,  $d_{15^\circ/4^\circ}$ , 0.89524.

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$	Calc.	Diff.
$H_a$	1.38442	0.42940	112.531	112.548	-0.015
$H_\beta$	1.39187	0.43773	114.717	114.710	+0.007
$H_\gamma$	1.39612	0.44247	115.959	115.964	-0.005

Percentage difference between observed and calculated values :

$H_\alpha$  0.013                       $H_\beta$  0.006                       $H_\gamma$  0.004

These differences are so small that the found and calculated numbers may be considered identical.

The refractive indices of the constituents of this mixture are also nearly identical, being for  $H^\alpha$  at  $15^\circ$

Heptane .....	1.38847.
Ethyl nitrate .....	1.38510
Difference .....	0.00337

The refractive power of the specimen of ethyl nitrate employed will be found on p. 288.

The heptane used was from *Pinus Sabiniana*, and its refractive power was determined in 1892 (Trans., 61, 294). It was, however, re-examined and the following is a comparison of the old and new molecular refractions :

	$H_\alpha$	$H_\beta$	$H_\gamma$
$\frac{\mu-1}{d} p$ old determination.....	56.451	57.461	—
„ new „ .....	56.481	57.462	58.018
Difference .....	+0.030	0.001	

*Mixture of Equal Volumes of Methylene Iodide and Ethyl Oxalate at  $15^\circ$ .*

Density,  $d_{15^\circ/15^\circ} = 2.18438$ ; the average density of the products unmixed at  $15^\circ/15^\circ$  is 2.21263, showing a difference due to expansion of +0.02825. The composition of the mixture is 1 mol.  $\text{CH}_2\text{I}_2$  + 0.596 mol.  $\text{EtNO}_3$ . Mol. wt., 355.102. Density,  $d_{15^\circ/4^\circ} = 2.18254$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$	Calc.	Diff.
$H_\alpha$ .....	1.55337	0.25354	90.034	91.953	1.919
$H_\beta$ .....	1.57322	0.26264	93.264	95.575	2.311
$H_\gamma$ .....	1.58628	0.26862	95.388	98.086	2.698

Percentage difference between observed and calculated values :

$H_\alpha$  2.087                       $H_\beta$  2.418                       $H_\gamma$  2.571.

Reduction in dispersion for  $H_\gamma - H_\alpha$  : Calc. .... 6.133  
Found..... 5.354

Difference ... 0.779

Differences of indices of refraction for  $H_a$  at  $15^\circ$ :

Methylene iodide .....	1.73500
Ethyl oxalate .....	1.41036
	<hr/> 0.32464

*Methylene Iodide*.—This substance was purified by freezing, and then rubbing the product upon a porous plate until free from oil; when melted, it was shaken with two or three drops of caustic potash to decolorise it, this was then soaked up with some dry potassium carbonate and the clear liquid filtered, finally it was treated with a little phosphoric oxide and again filtered. It was a pale yellow oil. Density,  $d_{15^\circ/15^\circ} = 3.3398$ ;  $d_{15^\circ/4^\circ} = 3.33699$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$
$H_a$ .....	1.73500	0.22026	59.029
$H_\beta$ .....	1.77266	0.23154	62.054
$H_\gamma$ .....	1.79957	0.23961	64.215

$H_\gamma$  was rather difficult to read. Dispersion  $H_\gamma - H_a = 5.186$ .

A previous determination of a specimen prepared as above, and then distilled under reduced pressure, gave  $H_a$  59.114. This was probably the purer product (Trans., 1892, 61, 296).

*Ethyl Oxalate*.—Boiling point,  $185^\circ$  (corr.); density,  $d_{15^\circ/15^\circ} = 1.08547$ ;  $d_{15^\circ/4^\circ} = 1.08456$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$
$H_a$ .....	1.41036	0.37837	55.242
$H_\beta$ .....	1.41781	0.38523	56.244
$H_\gamma$ .....	1.42216	0.38925	56.830

Dispersion,  $H_\gamma - H_a = 1.588$

*Mixture of equal volumes of Carbon Disulphide and Ethyl Nitrate at  $15^\circ$ .*

This mixture consists of 1 mol.  $CS_2$  and 0.733 mol.  $EtNO_3$ ; the molecular weight is 142.67. Density,  $d_{15^\circ/4^\circ} = 1.17388$ .

Line	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$	Calc.	Diff.
$H_a$ .....	1.49056	0.41790	59.621	60.277	-0.656
$H_\beta$ .....	1.51012	0.43456	61.998	62.815	-0.817
$H_\gamma$ .....	1.52272	0.44529	63.530	64.464	-0.934

Percentage difference between observed and calculated values.

$H_a$  - 1.083

$H_\beta$  - 1.330

$H_\gamma$  - 1.448

Reduction in dispersion for $H_a - H_\gamma$ : Calc. ....	4.187
Found.....	3.909
Difference ...	- 0.278

From these results, it is seen that, as in the case of the magnetic rotations, the refractive power of this mixture is considerably *less* than that calculated from its constituents, and that there is also a considerable falling off in the dispersion.

Difference between the indices of refraction for  $H_a$  at  $15^\circ$ .

Carbon disulphide .....	1.62207
Ethyl nitrate .....	1.38572
	<hr/> 0.23635
Average density, unmixed, $d\ 15^\circ/15^\circ$ ...	1.19390
„ „ mixed, $d\ 15^\circ/15^\circ$ .....	1.17487
Difference .....	<hr/> - 0.01903

*Carbon Disulphide.*—This was very carefully purified and redistilled from phosphoric oxide before examination. Density,  $d\ 16.8^\circ/4^\circ = 1.26839$ .

Line.	$\mu_{\frac{16.8^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
K .....	1.61077	0.48153	36.596
Li .....	1.61921	0.48818	37.102
$H_a$ .....	1.62087	0.48950	37.202
Na .....	1.63031	0.49694	37.767
$H_\beta$ .....	1.65513	0.51650	39.254
$H_\gamma$ .....	1.67786	0.53442	40.616

Dispersion,  $H_a - H_\gamma = 3.414$ .

*Ethyl Nitrate.*—This substance was treated in the cold with phosphoric oxide to remove any traces of alcohol or water, decanted from this, kept over anhydrous potassium carbonate for a few days, and finally distilled, the first part that came over being rejected. Density,  $d\ 16.2^\circ/4^\circ = 1.11315$ .

Line.	$\mu_{\frac{16.2^\circ}{4^\circ}}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
K .....	1.38242	0.34355	31.263
Li .....	1.38458	0.34548	31.439
$H_a$ .....	1.38509	0.34595	31.481
Na .....	1.38725	0.34788	31.657
$H_\beta$ .....	1.39320	0.35323	32.144
$H_\gamma$ .....	1.39799	0.35753	32.536

Dispersion  $H_a - H_\gamma = 1.055$ .

*Mixture of equal volumes of Benzene and Heptane at 15°.*

Density,  $d_{15^\circ/15^\circ} = 0.78278$ . Composition, 1 mol.  $C_6H_6 + 0.606$  mol.  $C_7H_{16}$ . Mol. wt., 138.65. Density,  $d_{15^\circ/4^\circ} = 0.78212$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$	Calc.	Diff.
$H_a$ .....	1.44063	0.56338	78.113	78.321	-0.208
$H_\beta$ .....	1.45221	0.57818	80.165	80.405	-0.240
$H_\gamma$ .....	1.45939	0.58736	81.438	81.675	-0.237

Reduction in dispersion for  $H_a - H_\gamma$ : Calc. .... 3.354  
Found..... 3.325

Difference ... -0.029

Percentage difference between observed and calculated values:

$H_a$  0.265       $H_\beta$  0.298       $H_\gamma$  0.290

Difference between the indices of refraction for  $H_a$  at 15°:

Benzene..... 1.49995  
Heptane ..... 1.38855

0.11140

Average density, unmixed,  $d_{15^\circ/15^\circ}$ , 0.78687

„ „ mixed,  $d_{15^\circ/15^\circ}$ , 0.78278

Difference due to expansion..... 0.00409

*Mixture of equal volumes of Bromonaphthalene and Ethyl Nitrate at 15°.*

Relative density,  $d_{15^\circ/15^\circ} = 1.30677$ . Average density, unmixed,  $d_{15^\circ/15^\circ} = 1.30465$ , showing a difference due to contraction of -0.00212. Composition 1 mol.  $C_{10}H_7Br + 1.7$  mols.  $EtNO_3$ . Mol. wt., 361.653. Density,  $d_{15^\circ/4^\circ} = 1.30567$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$	Calc.	Diff.
$H_a$ ...	1.51739	0.39626	143.310	143.948	-0.638
$H_\beta$ ...	1.53728	0.41150	148.819	149.610	-0.791
$H_\gamma$ ...	1.55040	0.42154	152.453	153.354	-0.901

Percentage difference between observed and calculated values:

$H_a$  0.4432       $H_\beta$  0.5287       $H_\gamma$  0.5875.

Reduction in dispersion for  $H_a - H_\gamma$ : Calc. .... 9.406

Found..... 9.143

Difference ... -0.263

Difference between indices of refraction for  $H_\alpha$  at  $15^\circ$ :

$\alpha$ -Bromonaphthalene .....	1.65186
Ethyl nitrate .....	1.38572
Difference .....	0.26614

*$\alpha$ -Bromonaphthalene.*—The  $\alpha$ -bromonaphthalene employed was obtained from Kahlbaum, and was purified only by fractional distillation. Boiling point,  $284$ — $286^\circ$  (corr.). Density,  $d_{15^\circ/15^\circ} = 1.49340$ ;  $d_{15^\circ/4^\circ} = 1.49214$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
$H_\alpha$ .....	1.65186	0.43686	90.431
$H_\beta$ .....	1.68455	0.45877	94.965
$H_\gamma$ .....	1.70673	0.47364	98.043

Dispersion,  $H_\gamma - H_\alpha = 7.612$ .

*Mixture of equal volumes of  $\alpha$ -Bromonaphthalene and Heptane at  $15^\circ$ .*

Density,  $d_{15^\circ/15^\circ} = 1.10062$ . Average density, unmixed,  $d_{15^\circ/15^\circ} = 1.09096$ , showing a difference, due to contraction on mixing, of  $0.00966$ . Composition of mixture, 1 mol.  $C_{10}H_7Br + 0.954$  mol.  $C_7H_{16}$ . Mol. wt.,  $302.443$ . Density,  $d_{15^\circ/4^\circ} = 1.09965$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$	Calc.	Diff.
$H_\alpha$ ...	1.52353	0.47608	143.988	144.336	-0.348
$H_\beta$ ...	1.54312	0.49390	149.377	149.807	-0.430
$H_\gamma$ ...	1.55594	0.50556	152.903	143.415	-0.512

Percentage difference between observed and calculated values:

$H_\alpha$  0.241       $H_\beta$  0.287       $H_\gamma$  0.333

Reduction in dispersion for  $H_\gamma - H_\alpha$ : Calc. .... 9.079

Found..... 8.915

Difference ... -0.164

*Mixture of equal volumes of Phenetole and Benzyl Cyanide at  $15^\circ$ .*

Density,  $d_{15^\circ/15^\circ} = 0.99653$ ; average density, unmixed,  $1.00888$ , showing expansion of  $0.01235$ . Composition, 1 mol.,  $C_8H_{10}O + 1.0975$  mol.,  $C_8H_7N$ . Mol. wt.,  $250.415$ . Density,  $d_{15^\circ/4^\circ} = 0.99569$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$	Calc.	Diff.
$H_\alpha$ .....	1.51320	0.51542	129.068	129.143	0.075
$H_\beta$ .....	1.52917	0.53146	133.086	133.162	0.076
$H_\gamma$ .....	1.53913	0.54146	135.590	135.657	0.067

Reduction in dispersion for  $H_\gamma - H_\alpha$ : Calc..... 6.514  
 Found ..... 6.522

Difference... +0.008

Percentage difference between observed and calculated values:

$H_\alpha$  -0.05       $H_\beta$  -0.06       $H_\gamma$  -0.05.

Difference between indices of refraction for  $H_\alpha$  at  $15^\circ$ :

Benzyl cyanide ..... 1.52068

Phenetole ..... 1.50551

0.01517

In the case of this mixture, where the refractive power of the two substances differ very little, it is seen that the numbers obtained are only very slightly lower than those calculated, and that there is no appreciable difference in the dispersion.

*Phenetole*.—Boiling point,  $170.3^\circ$  (corr.). Density,  $d$   $14.7^\circ/4^\circ = 0.96963$ .

	$\mu$ $14.7^\circ$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu-1}{d} p$ .
$H_\alpha$ .....	1.50563	0.52147	63.619
$H_\beta$ .....	1.52197	0.53832	65.674
$H_\gamma$ .....	1.53210	0.54877	66.950

Dispersion  $H_\gamma - H_\alpha = 3.331$ .

*Benzyl Cyanide*.—Boiling point,  $233.5^\circ$  (corr.). Density,  $d$   $15.2^\circ/4^\circ = 1.02025$ .

	$\mu$ $15.2^\circ$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu-1}{d} p$ .
$H_\alpha$ .....	1.52065	0.51028	59.703
$H_\beta$ .....	1.53625	0.52558	61.493
$H_\gamma$ .....	1.54594	0.53507	62.603

Dispersion  $H_\gamma - H_\alpha = 2.900$ .

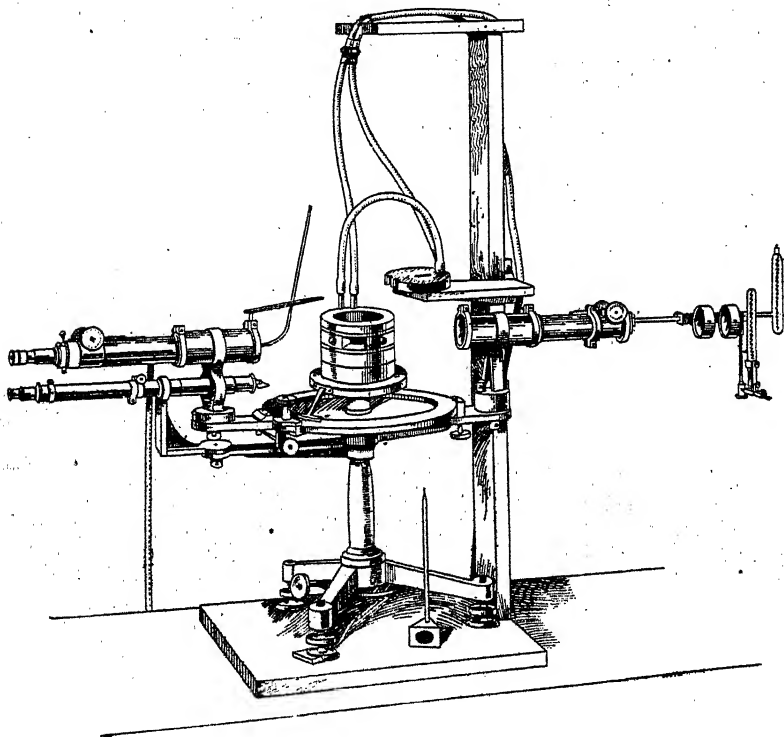
### III. IMPROVED SPECTROMETER SCALE READER.

The usual method of reading the scale and vernier of a spectrometer by means of a lens is far from convenient, as it requires the observer to change his position from that occupied when using the observing telescope for the spectrum lines each time he has to register the result; there is often a difficulty also in getting a satisfactory illumination of the scale, especially in a darkened room. The loss of time involved is very undesirable during a determination of the refractive indices of fluids in a hollow prism, particularly when the coefficients of expansion are large and readings are made for several lines of reference on both

sides of the prism, because accurate results can only be obtained if the temperature of the substance is kept *constant*.

To overcome these inconveniences an arrangement has been devised by which the scale and vernier are read by means of a long, narrow telescope, so arranged that its eye-piece is situated just below that of the observing telescope. The apparatus is shown in the figure and has been found to be convenient and to work very satisfactorily.

In this instrument, the support carrying the observing telescope has a slot through which the reading telescope passes, and this slot is



made wide enough to allow the latter to move to the right or left over rather more than the entire length of the vernier by about  $5^{\circ}$  on each side; both telescopes work from the central column which supports the circle. The reading telescope is provided at one end with a right-angle prism, which is not fixed, but supported by two screws, one on each side, so that its position can be changed by hand until the most convenient view of the scale and vernier is obtained; this prism is not placed directly over the scale, but sufficiently far back to avoid casting a shadow upon it. The illumination of the scale



and vernier is effected by means of a small gas jet fixed on the side of the observing telescope, and moving with it, the gas being supplied by means of a piece of rubber tubing sufficiently long to give freedom of movement; this gas supply is also provided with a by-pass so that it can be easily reduced and only sufficient light left for the small mirror used to illuminate the bright pointer in the eye piece of the observing telescope. A piece of ground glass is also fixed above the observing telescope to diffuse the light falling upon the scale and vernier, and thus facilitate the readings. The reading telescope can be drawn back out of the slot, moved to any part of the circle, and after being pushed back into position, used for readings in relation to the vernier of the table supporting the prism; when this is done it is well to hold a piece of ground glass in such a position that the light may pass through it on to the scale. Unless it is necessary to keep the observing telescope fixed in position, after reading the scale it is more convenient and simpler to loosen the clamp and move both telescopes to the position of this second vernier. The instrument is arranged to read to 30", which appears to be as small an amount as is useful in determining refractive indices.

A few remarks may be made in reference to other parts of the instrument shown in the figure. In this, the position of the copper cell (*Trans.*, 1892, 61, 287) is shown with its lid removed, and supported on a little shelf (which is generally turned up out of the way when not in use), ready to receive the prism, also the elastic tubes through which the water is circulated so as to keep the cell and prism at any desired temperature. The table supporting this cell and the prism can be rotated by hand to any desired position; it is, however, also provided with a fine adjustment passing up through the central column of the stand, and worked by a mill head at the foot of the stand. The arrangement for supporting the vacuum tube has also been found to be very convenient, especially when alternately using both the vacuum tube and Bunsen flame. The vacuum tube is not only held in position by the bar and clamp connected with the collimator tube, but the clamp itself slides on a small bar at right angles to the apparatus, having a spring on one side, and an adjusting screw on the other, so that its position in relation to the slit can be adjusted with precision; it can also be pressed back out of position and kept there by means of a milled head screw, whilst the Bunsen flame, coloured by potassium, lithium, sodium, or thallium salts, is used, and when liberated is pushed back into position without any further adjustment. Two cylinder lenses, crossing each other, are also used, as seen in the figure, and are found to be very useful, especially for upright vacuum tubes.

In making the observations of the lines of reference, a rather wide slit is used, because it is less trying to the eyes, and has been found

quite as accurate as a fine slit, provided all the measurements are made to the *fixed* side or jaw of the slit, and not to the centre of it, of course taking care to use this for both sides of the prism. The thermometer employed is divided to  $0.1^\circ$ , but this is none too fine. If the temperature is kept constant, independent determinations of molecular refractions are found to differ only very slightly in the second place of decimals.

## XXVII.—The Condensation of Formaldehyde with Ethyl Malonate, and Synthesis of Pentamethylene-1 : 2 : 4-tricarboxylic Acid.

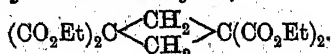
By J. FRANK BOTTOMLEY and W. H. PERKIN, jun.

IN a previous communication on the condensation of formaldehyde and ethyl malonate (Haworth and Perkin, Trans., 1898, 73, 330), it was shown that the following substances were formed either directly or indirectly during this process:

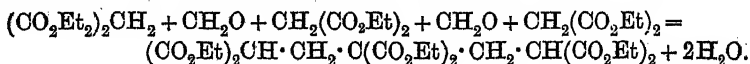
(1) *Ethyl methylenemalonate*,  $\text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et})_2$ , and two polymerides called respectively *ethyl paramethylenemalonate* and *ethyl metamethylenemalonate*.

(2) *Ethyl propanetetracarboxylate*,  $(\text{CO}_2\text{Et})_2\text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$ .

(3) *Ethyl tetramethylenetetracarboxylate*,

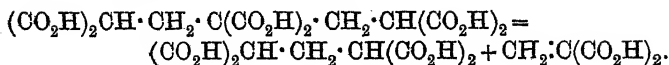


The further investigation of this condensation has again given interesting results, since it has been found that, under conditions different from those used in the first instance, the reaction takes place in such a way that 2 mols. of formaldehyde condense with 3 mols. of ethyl malonate and *ethyl pentanehexacarboxylate* is formed, thus:



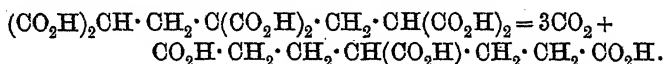
This new ester, which is solid and melts at  $53-55^\circ$ , is decomposed by boiling with baryta water, with formation of a syrupy polybasic acid which, when heated at  $240^\circ$ , loses carbon dioxide and yields *glutaric acid*.

This curious result may be explained on the assumption that, under the conditions employed, the hexabasic ester, or the hexabasic acid produced from it by hydrolysis, is decomposed into propanetetracarboxylic acid together with methylenemalonic acid or its decomposition products, thus:



The propanetetracarboxylic acid would then, at  $240^\circ$ , lose 2 mols. of carbon dioxide, with formation of glutaric acid.

When, however, ethyl pentanehexacarboxylate is boiled with dilute hydrochloric acid, the hydrolysis proceeds normally, and a syrupy acid is obtained which, on heating at  $200^\circ$ , is decomposed into carbon dioxide and *pentane- $\alpha,\gamma$ -tricarboxylic acid*,



This acid melts at  $113\text{--}114.5^\circ$ , and is doubtless identical with the acid melting at  $106\text{--}107^\circ$  which Emery (*Ber.*, 1891, 24, 284) obtained by hydrolysing ethyl pentanetetracarboxylate,

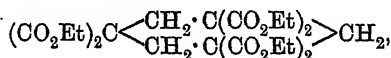


with alcoholic potash.

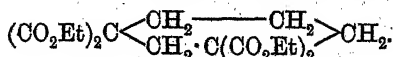
Being in possession of considerable quantities of ethyl pentanehexacarboxylate, we have submitted it to careful examination, and as its formula would indicate that it should form a disodium compound of the constitution



we, in the first place, endeavoured to obtain from it, by the action of sodium ethoxide and methylene iodide, the ethyl hexamethylenehexacarboxylate of the formula

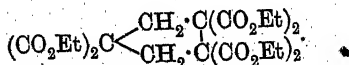


which, we have reason to believe, is one of the products formed when formaldehyde condenses with ethyl malonate. It was thought that there would be no difficulty in effecting this synthesis, since it has already been shown (Perkin, *Trans.*, 1891, 59, 803) that the disodium compound of the analogously constituted ethyl pentanetetracarboxylate,  $(\text{CO}_2\text{Et})_2\text{CNa}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CNa}(\text{CO}_2\text{Et})_2$ , when digested with methylene iodide, yields ethyl hexamethylenetetracarboxylate,

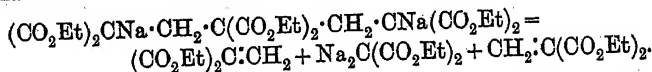


Curiously enough, we found that, when digested with sodium ethoxide and methylene iodide in alcoholic solution, or when dissolved in benzene and treated first with sodium and then with methylene iodide, ethyl pentanehexacarboxylate does not appear to yield any ethyl hexamethylenehexacarboxylate, but is entirely split up with formation of large quantities of *ethyl paramethylenemalonate*. This

remarkable result led us to believe that ethyl pentanehexacarboxylate was not capable of forming a disodium compound, but on investigating the point we find that it must yield this derivative, because, when treated in ethereal solution with sodium ethoxide and bromine at a low temperature, it is converted into *ethyl pentamethylenehexacarboxylate*, thus:

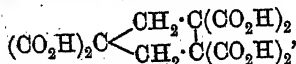


Possibly the disodium compound is only stable at a low temperature, and when heated to the temperature necessary to enable it to react with methylene iodide, decomposes with formation of 2 mols. of ethyl methylenemalonate and the disodium compound of ethyl malonate, thus:

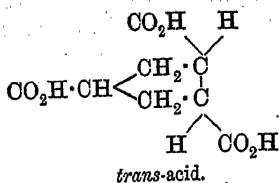
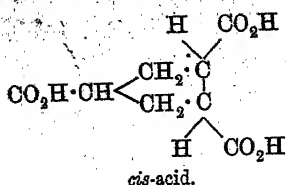


The disodium compound of ethyl malonate would then react with the methylene iodide to form a further quantity of ethyl paramethylenemalonate, and this would account for the large quantity of this ester which is formed when methylene iodide and sodium ethoxide react with ethyl pentanehexacarboxylate.

The ethyl pentamethylenehexacarboxylate mentioned above yields on hydrolysis *pentamethylenehexacarboxylic acid*,



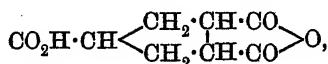
which melts at  $210^\circ$  with evolution of carbon dioxide and formation evidently of a mixture of the *cis*- and *trans*-modifications of *pentamethylenetricarboxylic acid*.



The method of preparing and separating these acids is explained on pp. 303—305.

The *trans*-acid appears to melt at  $127$ — $130^\circ$ , but this melting point may be too low, owing to the small amount of material at our disposal and to the very slight tendency to assume a definite crystalline form which this acid exhibits. When the *cis*-modification is heated in a capillary tube, it melts at  $146$ — $148^\circ$ , and if the temperature is raised above this point solidifies again, and the melting point is now found to be  $215$ — $217^\circ$ , a rather striking phenomenon which is due

to the acid being converted into *anhydro-cis-pentamethylenetricarboxylic acid*,\*



with loss of water, a behaviour which is not shown by the *trans*-modification. When treated with acetic anhydride and then distilled, the *cis*-acid also yields the anhydro-acid melting at 215—217°, which on treatment with water is again converted into the *cis*-acid.

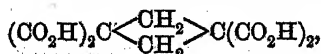
The *cis*-acid also differs from the *trans*-acid in forming a calcium salt which is sparingly soluble in cold water. Owing to the interest attaching to the carboxylic acids of pentamethylene, we propose, at a later date, to prepare these *cis*- and *trans*-tricarboxylic acids in larger quantities and to examine them more thoroughly.

During the course of our experiments on the condensation of formaldehyde with ethyl malonate, we gradually accumulated considerable quantities of the wax-like polymeride of ethyl methylenemalonate, which was described in the first communication (*loc. cit.*, p. 340) and which we called ethyl paramethylenemalonate.

We find that this polymeride crystallises well from alcohol, and as, by recrystallisation, we were able to obtain it in a condition slightly purer than the material which was used in our first experiments, we thought it well to repeat some of the remarkable decompositions previously described, and as a result we have been able in all cases to confirm the previous observations.

We find that pure *ethyl paramethylenemalonate* is decomposed on slow distillation almost completely into *ethyl methylenemalonate*, and that this, on standing, is rapidly converted into the horn-like polymeride called *ethyl metamethylenemalonate*. The horn-like polymeride is only very slowly decomposed on heating, but it also is ultimately converted almost quantitatively into *ethyl methylenemalonate*.

In the previous communication (*loc. cit.*, p. 343), it was stated that ethyl paramethylenemalonate, on hydrolysis with alcoholic potash, yielded an acid which was evidently *tetramethylenetetracarboxylic acid*,

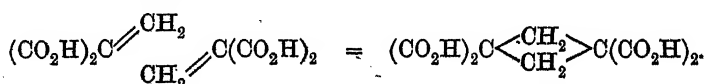


since, when heated at 180°, it was converted into *cis-tetramethylene-1:3-dicarboxylic acid* with loss of carbon dioxide. This synthesis of a tetramethylene ring is, as Michael (*J. pr. Chem.*, 1899, 60, 438) points out, the only case known of the formation of a 4-carbon ring by

\* It has been assumed in the formation of the anhydro-acid, and also in the case of the *cis-trans*-isomerism of the pentamethylenetricarboxylic acids, that the changes occur, as seems likely to be the case, in the succinic, and not in the glutaric, portion of the molecule.

polymerisation of an unsaturated substance. We have repeated these experiments, and can not only confirm the previous observation, but now find that the formation of the tetramethylene compound takes place apparently quantitatively, since we were unable to isolate any other product of the hydrolysis.

Ethyl paramethylenemalonate behaves therefore, on hydrolysis, as if it were the ester of tetramethylenetetra-carboxylic acid; the latter, however, has been prepared, and is an oil which distils without decomposition, that is to say, it has properties quite different from ethyl paramethylenemalonate, which is solid, and on distillation decomposes with formation of ethyl methylenemalonate. In endeavouring to obtain further experimental evidence to explain this difficulty, we have found that freshly distilled ethyl methylenemalonate, if hydrolysed before it has time to polymerise, also yields tetramethylenetetra-carboxylic acid. It is very probable that methylenemalononic acid is first produced during these hydrolyses, and, being incapable of existence under the conditions employed, spontaneously polymerises with formation of tetramethylenetetra-carboxylic acid,



If this explanation is correct, it is certainly remarkable that ethyl methylenemalonate does not polymerise in the same way with formation of ethyl tetramethylenetetra-carboxylate. It has, however, been repeatedly shown that this is not the case, and that the product of the polymerisation of the pure ester is the horn-like substance called ethyl metamethylenemalonate.

#### EXPERIMENTAL.

##### *Preparation of Ethyl Pentanehexacarboxylate,* $(\text{CO}_2\text{Et})_2\text{CH} \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et})_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$

As explained in the introduction, this substance is formed when ethyl malonate is condensed with formaldehyde under certain conditions, and in preparing it we have found the following method give good results.

A flask containing 96 grams of ethyl malonate and 30 grams of a 40 per cent. solution of formaldehyde is well cooled in ice, 1.5 grams of diethylamine then added, and after standing overnight the mixture is heated on a water-bath for 7 hours, and again allowed to stand until the next day. A large quantity of a crystalline product generally separates out, but if this does not happen, the mixture is cooled in a freezing mixture until crystallisation is complete, and the solid product

then separated from adhering oil by filtration on the pump and spreading on porous plates to drain. The oily filtrate, after being separated from the water contained in the formaldehyde solution and formed during the condensation, is distilled under 15 mm. pressure, and the following fractions collected :

100—180°. This consists chiefly of ethyl malonate and ethyl methylenemalonate.

180—210°. This consists chiefly of ethyl propanetetracarboxylate.

210—260°. This fraction, on standing, deposits crystals of ethyl pentanehexacarboxylate, which are separated from the oily impurity in the way explained above.

The yield obtained with the quantities of material stated above are approximately as follows :

Ethyl paramethylenemalonate .....	3 grams.
Ethyl pentanetetracarboxylate .....	25 „
Ethyl propanehexacarboxylate .....	48 „
Oils of high boiling point .....	10 „

During the course of a number of experiments which were instituted with the object of determining the conditions under which ethyl pentanetetracarboxylate is formed, it was found that the amount of diethylamine used had a very appreciable effect on the yield of this substance. Using 96 grams of ethyl malonate and 30 grams of formaldehyde solution in each case, the following results were obtained with varying quantities of diethylamine :

Diethylamine used .....	0.5	1.0	1.5 grams.
Ethyl pentanehexacarboxylate formed	32	43	48 „

*Ethyl pentanehexacarboxylate* crystallises from 70 per cent. alcohol in long, silky needles, and is very soluble in alcohol, ether, benzene, or glacial acetic acid. It melts at 53—55°, and distils almost without decomposition at 254—256° under 15 mm. pressure. On analysis :

0.1767 gave 0.3573 CO<sub>2</sub> and 0.1141 H<sub>2</sub>O. C=55.16 ; H=7.17.

0.1842 „ 0.3729 CO<sub>2</sub> „ 0.1182 H<sub>2</sub>O. C=55.20 ; H=7.13.

C<sub>25</sub>H<sub>36</sub>O<sub>12</sub> requires C=54.75 ; H=7.14 per cent.

*Hydrolysis of Ethyl Pentanehexacarboxylate by means of Hydrochloric Acid. Formation of Pentanetricarboxylic Acid,*  
 $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}.$

This hydrolysis, which proceeds normally, was conducted as follows. Ethyl pentanehexacarboxylate, in portions of 5 grams, was boiled on a sand-bath with a mixture of 10 grams of concentrated hydrochloric acid and 10 grams of water. After the boiling had been

continued for about 15 hours, and the oil had completely disappeared, the liquid was evaporated on the water-bath to a thick syrup, when it was noticed that carbon dioxide was given off in some quantity towards the end of the evaporation. The syrup was heated in a small flask in a paraffin bath at  $200^{\circ}$  until the evolution of carbon dioxide had ceased, the residue was then dissolved in water and boiled for some time with carefully purified animal charcoal. After filtering, the solution was concentrated, allowed to stand over sulphuric acid in a vacuum desiccator until a crystalline cake had formed, and the solid mass, which melted at  $100\text{--}110^{\circ}$ , further purified by crystallisation from a mixture of acetone and chloroform. *Pentanetricarboxylic acid* melts at  $113\text{--}114.5^{\circ}$ . On analysis:

0.1520 gave 0.2604  $\text{CO}_2$  and 0.0802  $\text{H}_2\text{O}$ .  $\text{C} = 46.73$ ;  $\text{H} = 5.86$ .

$\text{C}_8\text{H}_{12}\text{O}_6$  requires  $\text{C} = 47.05$ ;  $\text{H} = 5.88$  per cent.

The *silver* salt,  $\text{C}_8\text{H}_9\text{O}_6\text{Ag}_3$ , was obtained, on adding silver nitrate to the neutral solution of the ammonium salt, as a white, amorphous precipitate, which was analysed with the following result:

0.1627 gave, on ignition, 0.1 Ag.  $\text{Ag} = 61.48$ .

$\text{C}_8\text{H}_9\text{O}_6\text{Ag}_3$  requires  $\text{Ag} = 61.7$  per cent.

As already stated in the introduction, this acid is probably identical with Emery's pentanetricarboxylic acid melting at  $106\text{--}107^{\circ}$ .

*Action of Baryta on Ethyl Pentanehexacarboxylate. Formation of Glutaric Acid.*

In carrying out this curious decomposition, 40 grams of recrystallised ethyl pentanehexacarboxylate were boiled with an excess of baryta for about 6 hours. The thick, sparingly soluble barium salt which had separated was collected, washed with hot water, and carefully decomposed with dilute sulphuric acid, any slight excess of the acid being removed by adding small quantities of the barium salt, until the filtrate gave no precipitate with barium chloride. The barium sulphate was then filtered off and the solution evaporated on the water-bath, when a thick syrup was obtained which was transferred to a small flask and heated in an oil-bath at  $240^{\circ}$  until carbon dioxide ceased to be given off. The residue, which solidified on cooling, was dissolved in water, boiled with animal charcoal, and the solution, after filtration, evaporated on a water-bath to the consistency of a thick syrup.

On standing for some time in a vacuum desiccator, the syrup crystallised, and after spreading on a porous plate a white residue was obtained which crystallised well from benzene, melted at  $94\text{--}96^{\circ}$ , and had all the properties of glutaric acid. Analysis:



0.1635 gave 0.2723  $\text{CO}_2$  and 0.0946  $\text{H}_2\text{O}$ .  $\text{C} = 45.42$ ;  $\text{H} = 6.43$ .

$\text{C}_8\text{H}_8\text{O}_4$  requires  $\text{C} = 45.50$ ;  $\text{H} = 6.07$  per cent.

A small quantity of this acid was mixed with another specimen of glutaric acid, and the melting point of the mixed samples was found to be  $94-96^\circ$ . Another portion was neutralised with ammonia and a solution of zinc chloride added, when, on boiling, the characteristic zinc salt of glutaric acid separated.

*Action of Sodium Ethoxide and Methylene Iodide on the Disodium Compound of Ethyl Pentanehexacarboxylate. Attempt to prepare Ethyl Hexamethylenehexacarboxylate.*

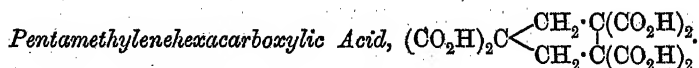
This experiment was carried out in two ways, namely, in alcoholic and in benzene solution:

I. Ethyl pentanehexacarboxylate (20 grams) was added to a solution of 1.85 grams of sodium in absolute alcohol; the whole was then heated on a water-bath in a reflux apparatus, and 10.6 grams of methylene iodide added, the flask being well shaken to promote thorough solution. After boiling for about 9 hours, the mixture, which was practically neutral, was freed as far as possible from alcohol by heating on the water-bath, water was then added, and the oil extracted with ether. The ethereal solution was washed well, dried with calcium chloride, the ether distilled off, and the oily residue fractionated under 15 mm. pressure. After a small quantity of unchanged methylene iodide had distilled over, the temperature rose rapidly to  $120^\circ$ , and a fraction was collected up to  $167^\circ$ , the greater part of which distilled between  $150^\circ$  and  $167^\circ$ . A small quantity came over between  $200^\circ$  and  $248^\circ$ , after which decomposition set in. The fraction  $120-167^\circ$ , on standing, became warm and solidified to a waxy mass which had exactly the appearance of ethyl paramethylenemalonate, and after recrystallising from absolute alcohol melted at  $148-150^\circ$ . Further investigation showed conclusively that this substance, which was obtained in considerable quantity, was ethyl paramethylenemalonate.

II. 10 grams of ethyl pentanehexacarboxylate were dissolved in about 600 c.c. of dry benzene, and to this solution 0.92 gram of sodium, which had previously been brought into a state of very fine division by melting under boiling xylene and shaking vigorously, was added. The mixture was then heated on the water-bath until all but the merest trace of the sodium had dissolved and a sticky mass of a sodium compound had begun to separate out on the sides of the flask. 5.3 grams of methylene iodide were then added, and the heating continued for some hours, when a copious precipitate of sodium iodide was deposited. After standing overnight, the benzene was distilled off and the residue treated as before. In this way, 10 grams of an

oil were obtained nearly all of which distilled between  $135^{\circ}$  and  $145^{\circ}$  under 15 mm. pressure, and soon solidified to a hard cake of ethyl paramethylenemalonate.

The formation of ethyl paramethylenemalonate in this way is very remarkable, and seems to show that it is not possible to prepare ethyl hexamethylenehexacarboxylate by the action of methylene iodide on the disodium compound of ethyl pentanehexacarboxylate.



The ester of this interesting acid is obtained when bromine acts on the disodium compound of ethyl pentanehexacarboxylate.

Sodium (1.83 grams) is dissolved in as small a quantity of absolute alcohol as possible, and the ethoxide, while still hot, is mixed with twice its volume of dry ether and, after cooling with ice, gradually added to an ethereal solution of ethyl pentanehexacarboxylate (20 grams). Bromine is then allowed to drop in slowly, with constant shaking, until the mixture has attained a light straw colour, all rise of temperature being carefully avoided. After standing for half an hour, the ethereal solution is well washed with water, dried over calcium chloride, and the ether distilled off, when a thick oil remains which, on distillation under 15 mm. pressure, yielded two fractions boiling at  $190$ – $215^{\circ}$  and  $230$ – $245^{\circ}$  respectively. During the distillation a considerable amount of decomposition took place.

The fraction boiling at  $190$ – $215^{\circ}$  was hydrolysed by boiling with an excess of baryta, the insoluble barium salt collected on the pump, well washed, mixed with boiling water, and decomposed exactly with sulphuric acid. After filtering from barium sulphate and evaporating the filtrate slowly on the water-bath, a thick syrup resulted which, on standing, partially crystallised. This crude product was left in contact with porous earthenware for some days until quite dry, and the hard, colourless mass thus obtained recrystallised from glacial acetic acid. The colourless crystals melted at  $210$ – $212^{\circ}$  with decomposition, and evidently consisted of *pentamethylenehexacarboxylic acid*. On analysis:

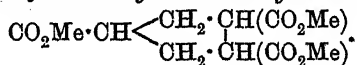
0.1509 gave 0.2147  $\text{CO}_2$  and 0.0393  $\text{H}_2\text{O}$ .  $\text{C} = 38.81$ ;  $\text{H} = 2.89$ .

$\text{C}_{11}\text{H}_{10}\text{O}_{12}$  requires  $\text{C} = 39.49$ ;  $\text{H} = 2.99$  per cent.

A silver salt was prepared in the usual way, but in attempting to determine the silver by heating in a crucible, the salt decomposed almost with explosive violence, being scattered out of the crucible. It was therefore decomposed by heating slowly to  $250^{\circ}$  in an air-bath and then igniting the residue in the usual way. The results obtained were

about 5 per cent. too low, showing that the silver salt was a mixture of the neutral salt with considerable quantities of acid salts. Similar difficulties have been observed in other cases in attempting to prepare pure neutral silver salts of polybasic acids.

*Preparation of Trimethyl Pentamethylenetricarboxylate,*



The yield of pure pentamethylenehexacarboxylic acid obtained by the method described in the last section was too small to allow of the tricarboxylic acids obtained from it by the elimination of carbon dioxide being examined in detail. We, however, ultimately found that the trimethyl ester of these acids could be prepared direct from the product of the action of bromine on the sodium compound of ethyl pentanehexacarboxylate in the following way.

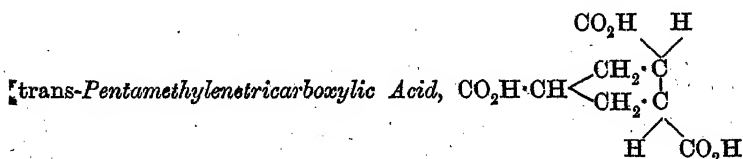
Ethyl pentanehexacarboxylate (100 grams) was treated as before with sodium ethoxide and bromine, and the crude product hydrolysed by boiling it with an excess of caustic potash dissolved in methyl alcohol. After the hydrolysis was complete, the bulk of the methyl alcohol was distilled off, water was then added, and the solution evaporated to remove the last traces of the alcohol. The concentrated solution was then acidified with excess of hydrochloric acid, evaporated to dryness, the residue mixed with sand and extracted for three days with pure ether in a Soxhlet apparatus. After distilling off the ether, the residual syrupy acid was heated in a paraffin-bath at  $200^\circ$  until carbon dioxide ceased to be given off, the sticky, dark-coloured mass mixed with 150 grams of methyl alcohol, then with 50 grams of concentrated sulphuric acid, and the whole heated for 7 hours on the water-bath. After standing overnight, the product was diluted with water and extracted several times with ether; the ethereal solution was then washed with water and dilute sodium carbonate, dried over anhydrous sodium sulphate, and the ether distilled off. The residual oil was fractionated under 15 mm. pressure, when two principal fractions were obtained boiling at  $100\text{--}130^\circ$  and  $167\text{--}170^\circ$ , which, after repeated refractionation, boiled ultimately at  $207\text{--}212^\circ$  under 760 mm., and at  $164\text{--}166^\circ$  under 12 mm. pressure respectively. The latter consisted of trimethyl pentamethylenetricarboxylate, as the following analysis shows:

0.2018 gave 0.3977  $\text{CO}_2$  and 0.1208  $\text{H}_2\text{O}$ . C = 53.75; H = 6.65.

$\text{C}_{11}\text{H}_{16}\text{O}_6$  requires C = 54.1; H = 6.57 per cent.

The oil boiling at  $207\text{--}212^\circ$  was also analysed, but the result gave no clue as to its constitution. On hydrolysis, it yielded a mixture of

acids which, by crystallisation, was roughly separated into two parts melting at 85—95° and 105—115° respectively. It seems likely that this mixture consisted of glutaric acid and tetramethylenedicarboxylic acid, but the quantity was too small for further examination.



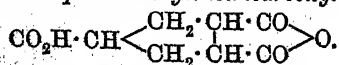
In preparing this acid, the trimethyl ester described in the last section was hydrolysed by boiling with excess of methyl alcoholic potash, water was then added, the methyl alcohol removed by evaporation on the water-bath, and the residue acidified with hydrochloric acid. After saturating with ammonium sulphate, the solution was extracted with pure ether, an operation which had to be repeated forty times before the whole of the acid was removed. The ethereal solution was then dried over anhydrous sodium sulphate, the ether distilled off, and the residue allowed to stand in a desiccator over sulphuric acid until it had completely solidified. In this way, 14 grams of a solid acid melting at 115—125°, and which was probably a mixture of the *cis*- and *trans*-modification of pentamethylenetricarboxylic acid, was obtained from 17 grams of the trimethyl ester. Unfortunately, this mixture is very difficult to crystallise, but ultimately repeated recrystallisation from concentrated hydrochloric acid yielded an acid which melted at 127—130° and was analysed with the following results:

0.1458 gave 0.2549  $\text{CO}_2$  and 0.0669  $\text{H}_2\text{O}$ .  $\text{C} = 47.66$ ;  $\text{H} = 5.1$ .

$\text{C}_8\text{H}_{10}\text{O}_6$  requires  $\text{C} = 47.5$ ;  $\text{H} = 4.95$  per cent.

This acid differs from *cis*-pentamethylenetricarboxylic acid described on p. 305, as it is not converted into an anhydro-acid melting at 217° when heated at 150—160°, and moreover forms a calcium salt which is soluble in cold water and precipitated on boiling the solution. We assume therefore that it is *trans*-pentamethylenetricarboxylic acid. When larger quantities have been prepared, it is possible that the melting point will be found to be higher than that given above.

*Anhydro-cis-pentamethylenetricarboxylic Acid,*



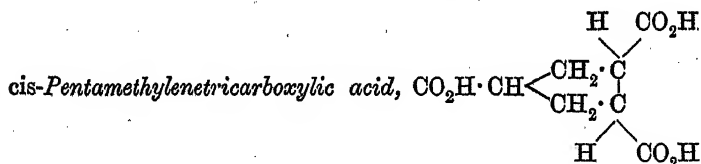
This well characterised substance was prepared in the following way. Crude pentamethylenetricarboxylic acid melting at 115—125°

was dissolved in four times its weight of acetic anhydride and boiled in a reflux apparatus for 2 hours. The whole was then transferred to a fractionating flask, and after the acetic anhydride had been distilled off at the ordinary pressure, the residue was distilled *as rapidly as possible* under 15 mm. pressure. A great deal of decomposition took place, but a considerable quantity of an oily distillate was nevertheless obtained, which, on cooling, solidified to distinct crystals mixed with some dark coloured impurity. The product was dissolved in a mixture of acetone and chloroform, the solution boiled with purified animal charcoal, and allowed to stand for some time, when crystals separated which, after twice recrystallising, were almost colourless. On analysis:

0.1360 gave 0.2592  $\text{CO}_2$  and 0.0585  $\text{H}_2\text{O}$ .  $\text{C} = 51.98$ ;  $\text{H} = 4.78$ .

$\text{C}_8\text{H}_8\text{O}_6$  requires  $\text{C} = 52.17$ ;  $\text{H} = 4.34$  per cent.

*Anhydro-cis-pentamethylenetricarboxylic acid* melts at  $215-217^\circ$ , and although it dissolves only sparingly in cold water, is sufficiently soluble to form a distinctly acid solution; it dissolves readily in boiling water and in cold dilute sodium carbonate solution.



This acid is formed by the action of water on anhydro-*cis*-pentamethylenetricarboxylic acid. 0.5 gram of the pure, finely powdered anhydro-acid was boiled for about an hour with water, and the solution evaporated on the water-bath until the acid began to crystallise out. After standing overnight in a vacuum desiccator, the crystals were spread on a porous plate, dried over sulphuric acid, and analysed, with the following result:

0.1519 gave 0.2643  $\text{CO}_2$  and 0.0700  $\text{H}_2\text{O}$ .  $\text{C} = 47.45$ ;  $\text{H} = 5.12$ .

$\text{C}_8\text{H}_{10}\text{O}_6$  requires  $\text{C} = 47.52$ ;  $\text{H} = 4.95$  per cent.

*cis*-Pentamethylenetricarboxylic acid melts at  $146-148^\circ$ ; at  $150-160^\circ$  it splits off water and solidifies, melting again at  $215-217^\circ$ , the melting point of the anhydro-acid. The calcium salt of this acid differs from that of the *trans*-derivative in being insoluble in cold water.

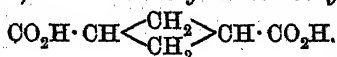
*Preparation of Ethyl Paramethylenemalonate.\**

The method employed for the preparation of this polymeride of ethyl methylenemalonate was practically the same as that described on p. 298 for the production of ethyl pentanehexacarboxylate, with the exception that the proportion of ethyl malonate and formaldehyde employed was different. As the result of several experiments, it was found that the best results were obtained by using 96 grams of ethyl malonate, 45 grams of 40 per cent. formaldehyde solution, and 1.5 grams of diethylamine.

After the condensation was complete, the product was distilled under 35 mm. pressure, and the following fractions collected :

I. 120—190°.      II. 190—230°.      III. 230—270°

The fraction 120—190° became warm on standing and slowly solidified to a waxy solid. This was spread on porous plates to remove adherent oil and crystallised from absolute alcohol, when pure ethyl paramethylenemalonate separated in the form of a colourless crystalline powder melting at 154—156°. The best yield obtained in this way was 22 grams of the crude dry product before crystallisation, but for some reason the yield varies very much in different operations, although the greatest care may be taken to reproduce in each case the same conditions.

*Hydrolysis of Ethyl Paramethylenemalonate with Alcoholic Potash.**Formation of cis-Tetramethylenedicarboxylic Acid,*

This hydrolysis, which has already been described (Trans., 1898, 73, 343), was repeated for reasons stated in the introduction to this paper. Carefully recrystallised ethyl paramethylenemalonate (20 grams) was boiled with a solution of 25 grams of caustic potash in methyl alcohol for about an hour. The methyl alcohol was distilled off as far as possible, water was then added, the solution boiled to remove the last traces of methyl alcohol, acidified with excess of hydrochloric acid, evaporated to dryness, and the solid residue, after mixing with sand, extracted in a Soxhlet apparatus with pure ether. The acid which remained, after distilling off the ether, was heated in a small flask at 200° until carbon dioxide ceased to be given off. The residue, which

\* By an unfortunate mistake, the amount of diethylamine used was omitted in the previous description of the condensation of formaldehyde with ethyl malonate (Trans., 1898, 73, 339); the amount used at that time was about 3 grams for the quantities of formaldehyde and ethyl malonate stated.

solidified on cooling, was dissolved in water, boiled with animal charcoal, filtered, and the filtrate concentrated and saturated with hydrogen chloride; nothing, however, separated until the solution was placed over solid potash in a vacuum desiccator, and then crystals gradually formed which melted at  $131-132^{\circ}$ , and consisted of *tetramethylene-1:3-dicarboxylic acid*. On analysis:

0.1459 gave  $0.2678 \text{ CO}_2$  and  $0.0748 \text{ H}_2\text{O}$ .  $\text{C} = 50.05$ ;  $\text{H} = 5.69$ .

$\text{C}_6\text{H}_8\text{O}_4$  requires  $\text{C} = 50.0$ ;  $\text{H} = 5.55$  per cent.

The amount of the acid obtained in this way was not actually determined, but it was considerable, and on carefully examining the mother liquors, we were unable to detect the presence of any other substance. This experiment confirms, therefore, the results obtained under different conditions on the former occasion.

*Distillation of Ethyl Paramethylenemalonate. Formation of Ethyl Methylenemalonate and of Ethyl Metamethylenemalonate.*

The distillation of ethyl paramethylenemalonate has already been described (Trans., 1898, 73, 341), but as the small amount of material employed had not been recrystallised, and as the distillation was conducted under the ordinary pressure, it was thought necessary to repeat the experiments with pure material on a larger scale and under different conditions. Pure recrystallised ethyl paramethylenemalonate (15 grams) was slowly distilled under 35 mm. pressure from an ordinary fractionating flask, when practically the whole passed over below  $220^{\circ}$ , two fractions, boiling respectively at  $140-190^{\circ}$  and  $190-210^{\circ}$ , being collected. It was noticed, especially during the early stages of the distillation, that a gas appeared to be given off, and that white fumes were formed which did not condense.

The fraction  $140-190^{\circ}$ , which had an irritating odour resembling that of formaldehyde, was immediately redistilled under the ordinary pressure, when nearly the whole of it passed over between  $205^{\circ}$  and  $210^{\circ}$ , and this, on standing, soon became quite warm and polymerised to the horny modification called *ethyl metamethylenemalonate*.

The fraction boiling at  $190-210^{\circ}$  under 35 mm. pressure was then examined, and on refractionation was found to distil almost completely between  $110^{\circ}$  and  $120^{\circ}$  under 30 mm. pressure, a result which seems to indicate that the liquid boiling at  $190-210^{\circ}$  under 35 mm. pressure still contained some ethyl paramethylenemalonate which had escaped decomposition during the first distillation. The boiling point,  $110-120^{\circ}$  under 30 mm. pressure, is approximately that of ethyl methylenemalonate, and since the fraction readily decolorised bromine,

there can be no doubt that it contained considerable quantities of this ester. It remained, however, as a perfectly mobile liquid for nearly a fortnight, which is remarkable, since ethyl methylenemalonate generally polymerises within a few minutes, and it would therefore appear that slight impurities are capable of arresting this polymerisation. On the addition of a small crystal of ethyl paramethylenemalonate to the oil, polymerisation commenced at once, but, curiously enough, the polymeride formed was the *meta*- and not the *para*-modification.

The remainder of the liquid was redistilled under atmospheric pressure, when nearly the whole passed over between  $202^{\circ}$  and  $210^{\circ}$ , but towards the end of the distillation the liquid in the fractionating flask became very thick, and seemed to polymerise. The distillate, on standing, polymerised to ethyl metamethylenemalonate, but before this took place a small quantity was analysed :

0.1748 gave 0.3534  $\text{CO}_2$  and 0.1077  $\text{H}_2\text{O}$ .  $\text{C} = 55.14$  ;  $\text{H} = 6.85$ .

$\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2$  requires  $\text{C} = 55.81$  ;  $\text{H} = 6.98$  per cent.

This result confirms the statement made in the previous communication (*loc. cit.*, p. 341), that ethyl paramethylenemalonate, on distillation, is resolved into the methylenemalonate,  $\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2$ .

#### *Distillation of Ethyl Metamethylenemalonate, and Hydrolysis of Ethyl Methylenemalonate.*

After the results obtained in the distillation of ethyl paramethylenemalonate, it seemed interesting to investigate the *meta*-polymeride in the same direction.

Ethyl metamethylenemalonate, which was so tough and hard that it had to be broken up with a knife and hammer, was very slowly distilled in a small fractionating flask under 32 mm. pressure, using a small air-bath to heat the flask. During the distillation, some white fumes were given off which did not condense. The whole distilled over between  $110^{\circ}$  and  $120^{\circ}$  leaving no residue, and on refractionating the distillate under the ordinary pressure, almost all boiled between  $204^{\circ}$  and  $210^{\circ}$ , but towards the end of the operation the small residue in the flask became very thick, and polymerisation seemed to be taking place. The oil boiling at  $204$ — $210^{\circ}$  was found to consist of ethyl methylenemalonate, showing that the *meta*-, like the *para*-polymeride, is, on distillation, resolved into simple molecules of the composition  $\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2$ . The bulk of the ethyl methylenemalonate obtained in this way was at once, and before it had had time to polymerise, mixed with excess of alcoholic potash and heated on the water-bath until hydrolysis was complete. After evaporating off the alcohol, the residue was dissolved in hydrochloric acid and extracted repeatedly with ether ; the ether



was distilled off and the residual syrup rapidly distilled at the ordinary pressure. Almost the whole passed over between  $250^{\circ}$  and  $270^{\circ}$  and partially solidified, and after crystallisation from hydrochloric acid, colourless crystals were obtained which melted at  $132-134^{\circ}$ . On analysis:

0.1023 gave 0.1901  $\text{CO}_2$  and 0.0530  $\text{H}_2\text{O}$ .  $\text{C} = 50.67$ ;  $\text{H} = 5.75$ .

$\text{C}_6\text{H}_8\text{O}_4$  requires  $\text{C} = 50.05$ ;  $\text{H} = 5.55$  per cent.

Examination of this acid showed that it was *cis*-tetramethylenedicarboxylic acid, and its formation seems to indicate that methylenemalononic acid is not capable of existence under the conditions mentioned above, but at once undergoes polymerisation.

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## XXVIII.—*Action of Fuming Nitric Acid on $\alpha$ -Dibromocamphor.*

By ARTHUR LAPWORTH and EDGAR M. CHAPMAN, Salter's Fellow in the Research Laboratory of the Pharmaceutical Society of Great Britain.

THE products obtained by acting on  $\alpha$ -dibromocamphor with nitric acid have already been investigated by several chemists. The reaction was first studied by Kachler and Spitzer (*Monatsh.*, 1883, 4, 554) who heated dibromocamphor with fuming nitric acid and obtained what they believed to be camphoronic and isocamphoronic acids, together with a neutral substance, which, as it gave on analysis numbers in agreement with those required for the formula  $\text{C}_{24}\text{H}_{38}\text{O}_{12}\text{N}_4\text{Br}$ , was probably therefore a mixture. More recently, Forster (*Trans.*, 1896, 69, 36), using still stronger acid, obtained a lactone,  $\text{C}_{10}\text{H}_{14}\text{O}_2\text{Br}_2$ , which he termed dibromocampholide, but does not state that he made any examination of the products which were soluble in water.

In a paper by the present authors (*Trans.*, 1899, 75, 86), the results of the investigation of the action of dilute nitric acid in presence of silver nitrate on  $\alpha$ -dibromocamphor were described, and it was shown that the products were homocamphoronic acid,  $\text{C}_{10}\text{H}_{16}\text{O}_8$ , an open chain acid whose true nature had not before been recognised, and a neutral substance,  $\text{C}_{10}\text{H}_{14}\text{O}_6\text{N}_2$ , which was thought to be in all probability the chief constituent of the neutral product obtained by Kachler and Spitzer. Camphoronic and isocamphoronic acids could

not be detected, and it appeared not unlikely that Kachler and Spitzer had been mistaken in supposing that these substances were formed, more especially as, in the description of their experiments, there is little which would serve to show that they were actually dealing with these acids and not with homocamphoronic acid in an impure condition.

This point appeared to us to be worthy of closer investigation, and the products obtained by treating  $\alpha$ -dibromocamphor with fuming nitric acid were therefore studied, more especially with the object of ascertaining whether homocamphoronic acid was formed in the reaction, and whether any appreciable quantity of camphoronic or isocamphoronic acid could be detected, as the formation of the latter in any quantity would be difficult to understand. It seems fairly certain that its presence in the oxidation product could only be due to the production of large quantities of camphor in the initial stage of the reaction; this possibility, however, appears to be entirely excluded, as Kachler and Spitzer did not observe the production of camphoric acid, which would, in this event, have been formed in much greater amount than isocamphoronic acid.

It may be briefly stated that the results which we have obtained confirm our belief that isocamphoronic acid is not formed in appreciable amount, as the copper precipitate from which Kachler and Spitzer obtained their acid yielded nothing but somewhat impure homocamphoronic acid.

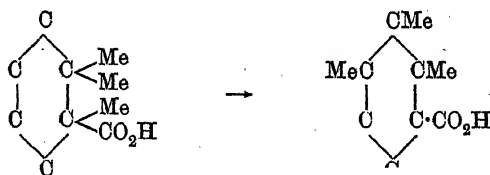
Camphoronic acid, contrary to our expectation, appeared to be produced in small quantity, but was mixed with homocamphoronic acid, and much difficulty was experienced in effecting a complete separation of the two substances, owing to the small amount of the former which is present. The production of camphoronic acid is not difficult to understand, as it might be produced by the oxidation of the homocamphoronic acid present, although we have not actually succeeded in effecting the direct conversion of the one into the other by means of fuming nitric acid.

Amongst the neutral products, which were practically insoluble in water, were dibromocampholide,  $C_{10}H_{14}O_2Br_2$ , the nitro-compound,  $C_{10}H_{14}O_6N_2$ , mentioned above, and also a small quantity of  $\alpha\alpha'$ -bromonitrocampbor,  $C_{10}H_{14}OBrNO_2$ , doubtless produced by the nitration of a small quantity of bromocamphor which is always formed in the first stage of the reaction. It now appears highly probable that the substance to which Kachler and Spitzer assigned the complicated formula  $C_{22}H_{30}O_{12}N_4Br$  already mentioned was a mixture of the two foregoing compounds.

After getting rid of nitric acid, an entirely new substance was found in the portion of the oxidation product which was soluble

in water. This was isolated by extracting the oily liquid containing the camphoronic and homocamphoronic acids with chloroform, in which these acids are insoluble. The substance thus obtained was evidently a lactone, and was not at all readily dissolved by pure water. It was easily hydrolysed by alkalis, and the acid which resulted was found to crystallise readily and had the composition  $C_{10}H_{16}O_4$ . Its exact nature was not ascertained, but as it was produced by the hydrolysis of a lactone, it was probably a hydroxy-acid; the function of the fourth oxygen atom is unknown, as the substance was not ketonic. All attempts to regenerate the lactone or to prepare an acetyl or benzoyl derivative were unsuccessful, as on each occasion where any action occurred the substance underwent a profound alteration, losing two molecular proportions of water, and was converted into an acid,  $C_{10}H_{12}O_2$ , which proved to be prehnitic acid, or 2 : 3 : 4-trimethylbenzoic acid.

It seems not unlikely that the acid  $C_{10}H_{16}O_4$  contains the grouping present in bromocamphorenic acid, and the change to the benzenoid compound would then involve loss of water and migration of two methyl groups into new positions. The relationship is seen very clearly if the groupings of the carbon atoms in the two sets of compounds are directly compared.



A substance having the formula  $C_{10}H_{16}O_4$ , and probably containing the former grouping, has already been obtained from dibromocampholide (Forster, *Trans.*, 1896, 69, 45), but the two compounds are not identical, as Forster's substance is characterised by its excessive solubility in water, whilst that obtained by us is only sparingly soluble in that medium; moreover, the former does not appear to undergo the interesting change to 2 : 3 : 4-trimethylbenzoic acid.

#### *Oxidation of $\alpha$ -Dibromocamphor.*

The oxidation was carried out with the help of the strongest fuming nitric acid which could be obtained. The action then commences spontaneously, and if too violent may be moderated by cooling; large quantities of material may thus be worked up at once without inconvenience. When the evolution of nitrous fumes became slow, the combined liquids from a number of experiments were poured into a

large quantity of water, the aqueous portion being afterwards separated from the undissolved oil by decantation.

The portion which did not dissolve in water was collected and triturated with alcohol, when it set to a paste of fine needles consisting of dibromocampholide; the oily mother liquor from this was not investigated, as we were more particularly interested in the acid portion of the oxidation product.

The aqueous portion was transferred to a retort and concentrated until the residue assumed a syrupy consistency. It was then freed from nitric acid by repeated dilution with water and evaporation to dryness on the water-bath.

After this treatment, it was found that on adding a large quantity of water to the residue a considerable quantity of a thick, yellow oil was deposited; this was collected, dissolved in alcohol, and the solution allowed to evaporate spontaneously. Some quantity of crystalline matter gradually separated and was easily resolved by mechanical means into two substances. One of these formed thick, brilliant prisms, melted at  $105^{\circ}$ , and was found to be ordinary bromonitrocamphor; the other crystallised in needles, melted at  $152^{\circ}$ , and was evidently dibromocampholide. The oily mother liquor was freed from alcohol by evaporation, and oxidised further with fuming nitric acid; it then furnished a considerable quantity of a white, semi-solid material, which, after crystallisation from methyl alcohol, was obtained in the form of beautiful, six-sided plates, which melted at  $93-94^{\circ}$  and had all the properties of the compound,  $C_{10}H_{14}O_6N_2$ , described in a previous paper (Trans., 1899, 75, 992).

The clear aqueous liquid from which the yellow oil had been separated was again evaporated nearly to dryness, but the residue refused to solidify even after several months. A few small, flattened crystals, however, made their appearance, but the quantity of these was too small to admit of close examination. Although dilution did not cause a further deposition of neutral substances, it was thought that the liquid contained a considerable quantity of anhydrohomocamphoronic acid, which would serve to prevent crystallisation; the whole was therefore extracted repeatedly with chloroform, in which the polybasic acids are insoluble. From this chloroform extract, a new substance was obtained, the properties of which are described later in this paper (p. 314).

The liquid, thus freed from much attendant impurity, still refused to deposit crystals, and was therefore subjected to the treatment which Kachler and Spitzer employed (*loc. cit.*). The method was more or less similar to that described by us in a former paper (Trans., 1899, 75, 993), but as the product in the present case was found to be of a more mixed nature, far more care was necessarily exercised.

The acid in solution, as in the former case, was precipitated by excess of boiling baryta water, and the filtrate, after neutralisation with sulphuric acid in presence of phenolphthalein as indicator, by excess of copper acetate. The precipitates thus obtained were worked up separately.

*Examination of the Barium Precipitate.*

The barium precipitate, from which Kachler and Spitzer state that camphoronic acid may be isolated, was decomposed by suspending it in boiling water and adding sulphuric acid drop by drop until no further precipitate was produced. In order to accumulate the camphoronic acid, the barium salt of which is more readily precipitated than is that of its homologue, the liberated acids were subjected to repeated precipitation with boiling baryta water, the barium salt obtained being then decomposed by means of sulphuric acid, and the acid carefully examined. In effecting the further separation of the two acids, advantage was taken of the fact that dry homocamphoronic acid is less soluble than camphoronic acid in cold ethyl acetate; the whole of the semi-crystalline material was therefore dried in a desiccator and triturated several times with cold ethyl acetate, the residue consisting of nearly pure homocamphoronic acid. The ethyl acetate solution was evaporated, when a flocculent mass of fine needles was obtained which melted indefinitely at  $150-160^\circ$ , and after solidification remelted indefinitely at  $115-120^\circ$ , that is to say, at a temperature much higher than that at which the anhydride of homocamphoronic acid fuses. A small quantity was dried in a vacuum and analysed:

0.2825 gave 0.5193  $\text{CO}_2$  and 0.1653  $\text{H}_2\text{O}$ .  $\text{C} = 50.1$ ;  $\text{H} = 6.5$ .

$\text{C}_9\text{H}_{14}\text{O}_6$  requires  $\text{C} = 49.5$ ;  $\text{H} = 6.5$  per cent.

$\text{C}_{10}\text{H}_{16}\text{O}_6$  „  $\text{C} = 51.7$ ;  $\text{H} = 6.8$ . „

These numbers are intermediate between those for camphoronic acid and homocamphoronic acid, and the whole behaviour of the material suggested that it was a mixture. It was therefore recrystallised once more from hot water, the most sparingly soluble portion being separated, dried in a vacuum, and analysed.

0.2561 gave 0.4693  $\text{CO}_2$  and 0.1441  $\text{H}_2\text{O}$ .  $\text{C} = 49.9$ ;  $\text{H} = 6.3$  per cent.

The acid therefore had approximately the composition of camphoronic acid, and it is practically certain that it consisted of that substance. It melted somewhat indefinitely, but after being heated at  $180^\circ$  for half an hour and then cooled, remelted at  $130^\circ$ , a temperature not far removed from the melting point of anhydrocamphoronic acid;

the anilic acid melted at 141—143°, whilst pure camphoronanilic acid melts at 145°.

The whole of the crystalline material from which camphoronic acid had been separated was heated at its decomposing point for 5 minutes; the residue was then distilled and examined for camphoronic acid, which was shown to be present by the isolation of its well-defined bromophenylhydrazone, melting at 194° (compare *Trans.*, 1899, 75, 1002). The crystalline acid from the barium precipitate consisted, therefore, for the most part of homocamphoronic acid and contained only a small quantity of camphoronic acid.

*Examination of the Copper Precipitate.*

The acids liberated from the insoluble copper salt were subjected to precipitation with excess of baryta water in order to remove as much homocamphoronic acid as possible; the acids in the mother liquor were set free by means of sulphuric acid, the liquid evaporated, and the residue then heated at 180° for half an hour in order to convert homocamphoronic acid into its anhydro-derivative. The product was then mixed with water and left for several days in order that any unstable anhydroisocamphoronic acid present might be decomposed; on filtering and evaporating the aqueous portion to dryness, the very small quantity of residue became nearly solid, but consisted of nearly pure homocamphoronic acid; it gave the following result on analysis:

0.1877 gave 0.3574 CO<sub>2</sub> and 0.1115 H<sub>2</sub>O. C=51.9; H=6.6.

C<sub>10</sub>H<sub>16</sub>O<sub>6</sub> requires C=51.7; H=6.9 per cent.

The anhydro-acid, undissolved by water, was recrystallised and found to consist of pure anhydro-homocamphoric acid, as it was homogeneous, melted at 186—187°, and on slow distillation yielded camphoronic acid.

*Acid, C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>.*

It has been mentioned that the liquid obtained by evaporating the aqueous solution of the mixed oxidation products contained a substance which did not separate on dilution, but which was easily extracted with chloroform. The substance was thus obtained as an oil which did not show any tendency to crystallise even after several weeks. It was found to be scarcely soluble either in pure water or in water containing sodium carbonate, and was therefore not an acid. When heated, however, it charred and yielded a crystalline sublimate which dissolved readily in warm sodium carbonate solution with effervescence. As its behaviour led us to believe that it was a lactone, it was shaken with strong aqueous potassium hydroxide containing a little alcohol, when it slowly and almost completely dissolved, yielding a

brown solution; this was filtered, extracted with chloroform to remove neutral substances, acidified with hydrochloric acid, and extracted with ether. The ethereal solution suddenly deposited crystals, and on sowing the remaining aqueous solution with these, a quantity of brilliant, prismatic crystals were deposited, which were collected, washed with a little ether, and crystallised first from acetone and finally from ethyl acetate.

A specimen was dried at  $100^{\circ}$  until constant in weight and analysed.

0.2163 gave 0.4736  $\text{CO}_2$  and 0.1565  $\text{H}_2\text{O}$ .  $\text{C} = 59.7$ ;  $\text{H} = 8.0$ .

$\text{C}_{10}\text{H}_{16}\text{O}_4$  requires  $\text{C} = 60.0$ ;  $\text{H} = 8.0$  per cent.

The basicity of the acid was determined by titration against standard soda; the equivalent found was 201, that required for a monobasic acid,  $\text{C}_{10}\text{H}_{16}\text{O}_4$ , being 200.

The substance is very sparingly soluble in cold water, but dissolves readily in dilute sodium carbonate solution, and is reprecipitated on addition of acids. It is sparingly soluble in ether, ethyl acetate, or cold acetone, but dissolves somewhat readily in hot acetone, and the solution, on cooling, deposits the substance in brilliant, transparent crystals of considerable size, which belong, apparently, to the orthorhombic system; these crystals appear to contain solvent of crystallisation, as when heated at  $100^{\circ}$  they become opaque and gradually lose in weight. It is very sparingly soluble in benzene or chloroform and practically insoluble in light petroleum. It melts quite sharply at  $177^{\circ}$ , and after solidification melts again at this temperature.

When melted between slips of glass, it solidifies in a very characteristic manner from a large number of centres, and, owing to large contraction on cooling, interstices filled with air separate the various nuclei, which are thus usually isolated from one another. Examined in polarised light, the nuclei are seen to be surrounded by radiate aggregates of minute needles, and each of these shows a marked dark cross. Owing to the small size of the needles, the crystallographic nature of the individual crystals could not be ascertained.

The acid is saturated, as its solution in chloroform does not decolorise one of bromine in the same liquid; moreover, a solution of the acid in sodium carbonate does not affect a dilute solution of potassium permanganate, even on warming. It is not attacked by bromine, even when the substances are heated together in an open vessel. It is very stable towards the ordinary oxidising agents, is not appreciably affected by hot dilute chromic acid mixture, and may be boiled with moderately strong nitric acid for some time without undergoing noticeable oxidation.

As it is obtained from a neutral substance by means of potash, it

probably contains a hydroxyl group, but it was not found possible to obtain an acetyl derivative or to transform it into a lactone. All attempts to produce these effects either did not alter the substance or resulted in the curious change described later. The acid is not ketonic, as it does not yield an oxime or a phenylhydrazone.

*Action of Dehydrating Agents on the Acid  $C_{10}H_{16}O_4$ . Formation of Trimethylbenzoic Acid.*

When the foregoing acid, heated at  $180^\circ$  with water, is distilled, or is warmed with moderately strong sulphuric acid, it loses water, yielding an acid identical with that obtained by distilling the crude lactone. The change may also be brought about by boiling with acetyl chloride, but is best effected by warming the substance with hydrobromic acid; in the last-mentioned case, the substance quickly dissolves, forming a clear solution for a few seconds, but almost immediately afterwards a separation of fine needles commences and continues until the whole is transformed into a paste of these crystals. The substance obtained in this manner was purified by crystallisation from ethyl acetate, dried at  $100^\circ$ , and analysed:

0.2455 gave 0.6549  $CO_2$  and 0.1619  $H_2O$ .  $C = 72.8$ ;  $H = 7.3$ .

$C_{10}H_{12}O_2$  requires  $C = 73.2$ ;  $H = 7.3$  per cent.

This acid is sparingly soluble in boiling water, but dissolves readily in dilute aqueous sodium carbonate, producing effervescence, and is reprecipitated unchanged by acids. It dissolves fairly freely in glacial acetic acid, alcohol, or acetone, and is soluble to some extent in chloroform or benzene, but appears to be insoluble in light petroleum. It crystallises from ethyl acetate in large, transparent needles, the terminations of which are always jagged and devoid of crystal faces.

The substance melts sharply at  $167-168^\circ$ , and when heated strongly sublimes with very little decomposition. It is slightly volatile in steam, to which it imparts a characteristic odour.

When melted between slips of glass, it solidifies in semi-transparent patches showing aggregate polarisation. In convergent polarised light, the acute bisectrix of a biaxial interference figure is observed here and there, emerging normally to the field. The double refraction is strong and negative, and the dispersion is weak.

When excess of bromine is added to the dry substance, action readily takes place on warming, hydrogen bromide being evolved; the product crystallises readily from acetic acid in beautiful, satiny needles melting at  $213-215^\circ$ .

In order to determine, if possible, the constitution of the acid, the calcium salt was intimately mixed with soda-lime and heated in a



hard glass tube. A mixture of water and an insoluble oil was thus obtained, and the latter was separated, dried over sodium, and distilled; it boiled practically constantly at  $174-176^{\circ}$ . On analysis:

0.2035 gave 0.6676  $\text{CO}_2$  and 0.1831  $\text{H}_2\text{O}$ .  $\text{C} = 89.5$ ;  $\text{H} = 9.9$ .

$\text{C}_9\text{H}_{12}$  requires  $\text{C} = 90.0$ ;  $\text{H} = 10.0$  per cent.

The hydrocarbon was violently attacked by cold dry bromine, and after removing the excess of the latter by evaporation, a solid product was obtained which crystallised from alcohol in beautiful, glistening needles melting at  $242-243^{\circ}$ . The bromo-derivative gave the following result on analysis:

0.1575 gave 0.2510  $\text{AgBr}$ .  $\text{Br} = 67.9$ .

Calculated for  $\text{C}_9\text{H}_7\text{Br}_3$ ,  $\text{Br} = 67.3$  per cent.

The properties of the hydrocarbon and its bromo-derivative indicated that it was hemimellitene or 1:2:3-trimethylbenzene. Jacobson (*Ber.*, 1886, 19, 2517) gives the boiling point of hemimellitene as  $174-175.5^{\circ}$ , and the melting point of the tribromo-derivative as  $245^{\circ}$ . In order to make the identification complete, the hydrocarbon was warmed with sulphuric acid, in which it dissolved readily, and after getting rid of the sulphuric acid by means of barium carbonate in the usual way, the barium salt of the sulphonic acid was converted into the sodium salt, and this, by treatment with phosphorus pentachloride and ammonia, was transformed into the sulphonamide. The latter is very characteristic, and crystallises in small, compact forms which aggregate together, producing long columns resembling prisms; it melted sharply at  $194^{\circ}$ . Jacobson (*loc. cit.*) gives the melting point of hemimellitene-sulphonamide as  $196^{\circ}$ .

The constitution of the hydrocarbon having thus been ascertained, no difficulty was found in identifying the acid from which it was obtained as prehnitic acid or 2:3:4-trimethylbenzoic acid, as it agrees closely in melting point and general properties with the acid obtained by Jacobson from 1:2:3:4-tetramethylbenzene (*Ber.*, 1886, 19, 1214).

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XXIX.—*The Absorption Spectra of Ammonia, Methylamine, Hydroxylamine, Aldoxime, and Acetoxime.*

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It was shown by L. Soret that commercial ammonia, even after many recrystallisations as sulphate, still shows an absorption band. Hartley and Huntington (*Phil. Trans.*, 1879, Part I, 267) confirmed this observation, and, believing the absorption to be due to traces of some constituent of gas-liquor, examined specimens of what was sold as "volcanic" ammonia of special purity for analytical purposes. Three separate samples were examined, each measuring half a gallon, with the result that all the rays beyond  $1/\lambda$  2638.2 ( $\lambda$  2747.7) were absorbed by the strong solution in a cell 15 mm. in thickness. A very distinct absorption band was visible on diluting the liquid with eight volumes of water, and was still seen until sixteen volumes had been added.

This result appeared remarkable in view of the fact that gaseous ammonia, at atmospheric pressure, in a tube 1 metre in length, showed no selective absorption, and that ethylamine, even when solutions containing as much as 33 per cent. of the base were examined in cells 25 mm. in thickness, transmitted continuous spectra with very little absorption.

Carbamide also showed no absorption band, but transmitted a continuous spectrum.\* A 10 per cent. solution of carbamide in a cell 15 mm. in thickness transmits all rays to  $\lambda$  2140, rays more refrangible than  $\lambda$  2750 being slightly weakened.

When we remember that practically all the ammonia of commerce is obtained from coal tar, and is liable to contain minute traces of the volatile bases of the pyridine and other series, which can only be completely separated with great difficulty, it is obvious that great care must be taken to obtain chemically pure ammonia for examination before any trustworthy conclusion can be arrived at as to the character of its absorption spectrum.

The following investigation was undertaken with the view of definitely ascertaining whether or not chemically pure ammonia shows selective absorption. An examination of ordinary aqueous ammonia was first made in order to determine the exact position of its absorption band. A tube 150 mm. long was used. With this thickness of layer, a solution containing 5 grams of ammonia in 100 c.c. water showed complete absorption beyond  $1/\lambda$  3638 ( $\lambda$  2749). A

\* From unpublished experiments on the determination of aromatic substances in urine. See note *Dublin Journal of Medical Science*, June, 1882.—W. N. HARTLEY.

layer of the same thickness containing 2.5 grams of ammonia in 100 c.c. gave a continuous spectrum to  $1/\lambda$  3694 ( $\lambda$  2707), a broad absorption band occupying that portion of the spectrum which lies between  $1/\lambda$  3694 ( $\lambda$  2707) and  $1/\lambda$  4306 ( $\lambda$  2322), the spectrum again showing beyond this point. This band is persistent, being still traceable in a solution containing only 0.625 gram of ammonia in 100 c.c. All the samples of commercial ammonia examined showed selective absorption, but by converting the base into ammonium chloride, the absorption band was found to become less marked in the spectrum after successive crystallisations of the salt.

In order to try the effect of crystallisation of one of the less soluble salts, ammonia was converted into oxalate and the salt repeatedly crystallised. The oxalate was distilled with pure potassium hydroxide and the ammonia absorbed in pure distilled water, the spectrum of which was photographed on the same plate as that of the ammonia solution. Much greater thicknesses of liquid were examined than in previous experiments.

A layer 200 mm. thick of a solution containing 10.6 per cent. of ammonia prepared in this way from oxalate transmitted all rays to  $1/\lambda$  3638 ( $\lambda$  2749), but the spectrum was feeble from  $1/\lambda$  2738 ( $\lambda$  3652) to  $1/\lambda$  3638 ( $\lambda$  2749). No band was visible. A layer 100 mm. thick transmitted the rays to  $1/\lambda$  4323 ( $\lambda$  2313), but the spectrum was very feeble beyond  $1/\lambda$  3904 ( $\lambda$  2561).

From another portion of the purified oxalate the liberated ammonia was passed into optically pure hydrochloric acid; the ammonium chloride recrystallised several times was then examined, the solution of the salt employed having the same thickness of layer and containing the same amount of ammonia as that previously used in determining the position of the absorption band in ordinary ammonia. It now showed no trace of selective absorption, the spectrum being continuous to  $1/\lambda$  4666 ( $\lambda$  2143) with a scarcely perceptible weakness at the extreme ultra-violet end. Pure ammonia may therefore be obtained without difficulty by the decomposition of a crystallised ammonium salt such as the oxalate.

#### *Ammonia obtained from Hydroxylamine.*

Ammonia obtained by the reduction of hydroxylamine was next examined. Hydroxylamine hydrochloride was reduced with a zinc-copper couple and the ammonia distilled into pure hydrochloric acid; the ammonium chloride thus obtained was subsequently purified by recrystallisation.

A layer of 150 mm. of a solution containing 2.5 grams ammonia in 100 c.c. distilled water showed a continuous spectrum to  $1/\lambda$  4411

( $\lambda$  2267); the spectrum is weak from  $1/\lambda$  3886 ( $\lambda$  2573), but there was no indication of selective absorption.

As therefore neither ordinary ammonia, which has been carefully purified by the above method, nor ammonia obtained by the reduction of hydroxylamine, shows selective absorption, we conclude that the absorption band of ordinary ammonia is due to the presence of traces of foreign substances which distil over with it from the gas liquor.

We next endeavoured to ascertain the nature, and estimate the amount, of the impurity to which the band of ordinary aqueous ammonia is due. The position of the band seemed to indicate the pyridine bases as the most likely cause of the absorption, and, in fact, we found that a layer of 150 mm. thick of a solution containing 7.68 grams of pure ammonium chloride (equivalent to 2.5 grams of ammonia) and 0.00001 gram of pyridine in 100 c.c. water, showed almost exactly the same amount and character of absorption as a layer of ordinary aqueous ammonia of the same thickness and strength.

In a further experiment, we found that the addition of the same amount of pyridine (in the form of hydrochloride) to 100 c.c. of distilled water produced an identical result, the spectrum being hardly distinguishable from that of ordinary aqueous ammonia.\* It follows, therefore, that the strong ammonia used (35 per cent.  $\text{NH}_3$ ) contains approximately 0.00014 per cent. pyridine.

Although pyridine is thus shown to be the principal cause of the absorption, minute traces of its higher homologues and of volatile bases of other series are also probably present, as the slight differences between the spectrum of ordinary ammonia and that of pure pyridine appear to indicate.

#### *Methylamine Hydrochloride.*

Methylamine was investigated by Hartley and Huntington in cells 50 mm. thick (*Phil. Trans.*, 1879, Part I, 267).

An aqueous solution of methylamine was converted into hydrochloride and the salt purified by repeated recrystallisation. A layer 150 mm. thick of a solution containing 25 grams of methylamine as hydrochloride in 100 c.c. distilled water showed practically no absorption. There was a slight weakening of the spectrum towards the ultra-violet end, and one or two of the lines at the extreme end of the ultra-violet were cut off.

\* In this connection, it is interesting to note that, although a solution containing 0.00001 gram pyridine in 100 c.c. distilled water no longer showed an actual gap in the spectrum, there was a perceptible weakening of the lines of that portion of the spectrum in which the band of ordinary aqueous ammonia occurs.

*Hydroxylamine Hydrochloride.*

The hydroxylamine hydrochloride examined was subjected to repeated recrystallisation. It gave no precipitate with platinic chloride in presence of alcohol and ether, and it was therefore assumed to contain no ammonium chloride. The salt is highly diactinic and shows no trace of selective absorption. A layer 150 mm. thick of the solution containing 5 grams of hydroxylamine in 100 c.c. water gives a continuous spectrum to  $1/\lambda$  4125 ( $\lambda$  2424). A layer of the same thickness containing 2.5 grams in 100 c.c. water transmits the whole spectrum with the exception of a few of the lines at the extreme end of the ultra-violet.

*Acetaldoxime*,  $\text{CH}_3\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ .

Acetaldoxime was prepared in the usual manner by the action of aldehyde ammonia on hydroxylamine hydrochloride, and afterwards purified by fractional distillation until the boiling point was constant; it boiled at 114—115°. In solution, this compound shows no selective absorption, but very considerable general absorption. A layer 150 mm. thick of a solution containing 125 grams of acetaldoxime in 100 c.c. water absorbs all lines beyond  $1/\lambda$  3323 ( $\lambda$  3009). A layer 25 mm. thick of a solution containing 1 milligram-mol. in 20 c.c. water gives a continuous spectrum to  $1/\lambda$  3952 ( $\lambda$  2530) and a layer 1 mm. thick of the same solution shows a continuous spectrum to  $1/\lambda$  4417 ( $\lambda$  2264).

*Acetoxime*,  $(\text{CH}_3)_2\text{C}\cdot\text{N}\cdot\text{OH}$ .

Acetoxime was prepared in the usual manner by the action of hydroxylamine hydrochloride on acetone, and was purified by repeated recrystallisation from water; it melted at 59—60°.

Like acetaldoxime, acetoxime shows no selective absorption, but general absorption, which is slightly greater than in the case of the former substance, as was to be anticipated from the presence of an additional methyl group. A layer 25 mm. thick of a solution of acetoxime containing 1 milligram-mol. in 20 c.c. shows a continuous spectrum to  $1/\lambda$  3886 ( $\lambda$  2573); a layer 1 mm. thick of the same solution to  $1/\lambda$  4125 ( $\lambda$  2424).

The substances above referred to afford an excellent illustration of the intimate relation between the character and extent of absorption and the constitution of an organic compound. Ammonia is highly diactinic. The substitution of a methyl group for one of the hydrogen atoms has the effect merely of very slightly increasing the amount of continuous absorption of the most refrangible rays. Again, the substitution of hydroxyl for hydrogen has a similar effect, the group OH, however, having a greater absorptive power than the group CH<sub>3</sub>.

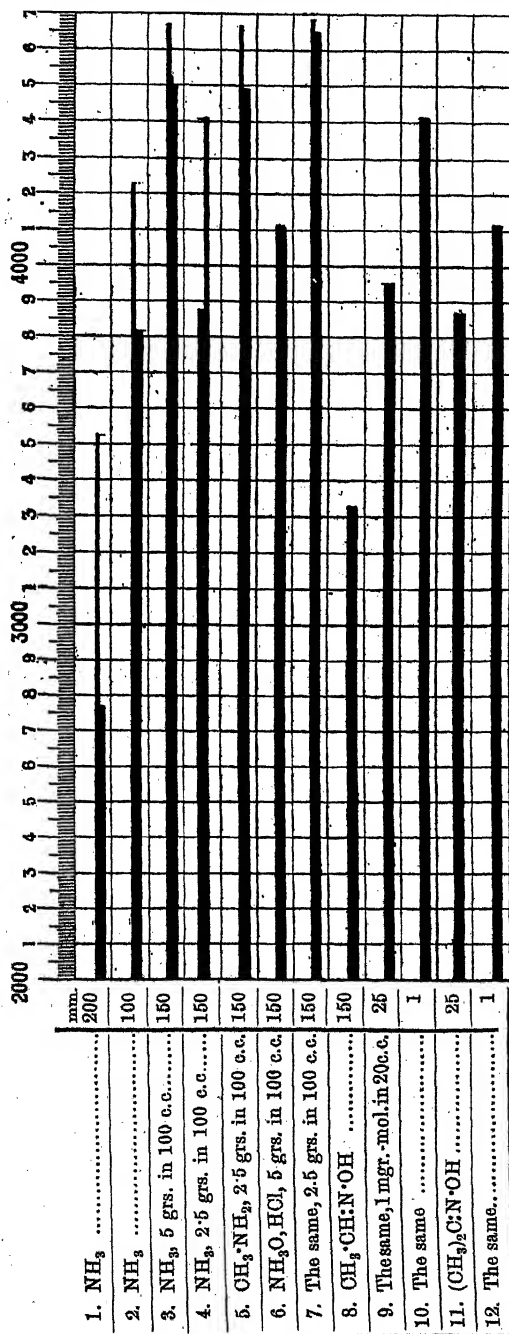
When we come to acetaldoxime and acetoxime, we find that, regarding them as derivatives of hydroxylamine, the introduction of the more complicated groups  $\text{:CH}\cdot\text{CH}_3$  and  $\text{:C}(\text{CH}_3)_2$  respectively for the two remaining hydrogen atoms of the original ammonia molecule, is accompanied by a great increase in the amount of the general absorption. Comparing however, acetaldoxime with acetoxime, the latter, which differs from the former in the possession of an additional methyl group, shows only slightly greater absorption. This is in harmony with previous observations on  $\text{CO}_2\text{H}$  groups, and the slightly increased absorption caused by the introduction of methyl groups for hydrogen atoms; also the stronger absorption caused by the replacement of hydrogen atoms by hydroxyl radicles.

A diagram drawn to a scale of oscillation frequencies shows at a glance the length of spectrum transmitted by these substances in different proportions, and through different thicknesses.

#### EXPERIMENTAL.

Most of the solutions examined were contained in a glass tube 150 mm. long, ground at the ends and closed with quartz discs held in position by means of brass rings, screwed to the ends of a metal tube, in which the glass tube was placed. The quartz discs were thus pressed firmly against the ends of the glass tube, an indiarubber washer being inserted between the disc and the brass ring. By this arrangement, the ends of the tube were rendered quite water-tight, whilst the solution was not brought into contact with anything but the glass and quartz discs. A hole drilled in the side of the glass tube, having a corresponding opening in the outer metal case, served for the introduction of the solution. After each experiment, the discs were removed from the ends of the tube, the tube removed from the metal case and thoroughly washed out. One tube, 200 mm. long, had the quartz ends cemented on by pressing the discs against the ground ends of the tube and dipping it in solid paraffin, just raised above its melting point. The percentages referred to in the paper represent in every case the number of grams of ammonia ( $\text{NH}_3$ ) in 100 c.c. of solution. The electrodes used, consisted, one of an alloy of cadmium and lead, the other of an alloy of cadmium and tin. By this arrangement, which was first fully described by one of us in 1885, and has been very generally used ever since, a large number of easily recognisable reference lines are obtained, since the cadmium lines, when the spark is of a suitable length, stretch across the whole width of the spectrum, whilst those of lead and tin only reach half way across. For the table of wave-lengths and positions of the 69 or 70 reference lines, compare Hartley, *Phil. Trans.*, 1885, Part II., 471, also article Spectroscope in Thorpe's Dictionary of Applied Chemistry.

Scale of Oscillation Frequencies.



No. 1. Ammonia obtained from recrystallised oxalate containing 10.6 per cent. of  $\text{NH}_3$ . Thickness 200 mm.

2. The same, rays transmitted through half the thickness.

3. Ammonia as ammonium chloride purified by repeated crystallisations. Thickness 150 mm.

4. Ammonia obtained by the reduction of hydroxylamine examined as ammonium chloride. Thickness 150 mm.

5. Methylamine as hydrochloride. Thickness 150 mm.

6. Hydroxylamine as hydrochloride. Thickness 150 mm.

7. The same half the quantity in solution.

8. Acetaldo 125 grs. in 100 c.c. Thickness of 150 mm.

9. The same 1 milligram-molecule in 20 c.c. Thickness of 25 mm.

10. The same 1 milligram-molecule in 20 c.c. Thickness of 1 mm.

11. Acetoxim, 1 milligram-molecule in 20 c.c. Thickness of 25 mm.

12. The same 1 milligram-molecule in 20 c.c. Thickness of 1 mm.

*Absorption Spectrum of the Distilled Water and Hydrochloric Acid used in the Experiments.*

The distilled water used for these experiments transmitted a continuous spectrum to  $1/\lambda$  4555 ( $\lambda$  2195), a line being visible at  $1/\lambda$  4662 ( $\lambda$  2145) when a layer 200 mm. in thickness was examined.

A normal solution of the hydrochloric acid used, 200 mm. in thickness, transmits all rays to  $1/\lambda$  4838 ( $\lambda$  2067) and strongly to  $1/\lambda$  4413 ( $\lambda$  2266).\*

(1)

*Ordinary Aqueous Ammonia.*

Thickness of layer of solution = 150 mm.

Strength of solution.	Description of spectrum.
2.5 per cent. ....	Spectrum continuous to $1/\lambda$ 3694 ( $\lambda$ 2707). <b>Absorption Band</b> $1/\lambda$ 3694—4306 ( $\lambda$ 2707—2322). Faint spectrum beyond $1/\lambda$ 4306 ( $\lambda$ 2322) with lines showing distinctly at $1/\lambda$ 4306 ( $\lambda$ 2322), $1/\lambda$ 4321 ( $\lambda$ 2314), $1/\lambda$ 4368 ( $\lambda$ 2289), and $1/\lambda$ 4415 ( $\lambda$ 2265). Complete absorption beyond.
1.25 per cent. ....	Spectrum almost continuous to $1/\lambda$ 4415 ( $\lambda$ 2265), but weak beyond $1/\lambda$ 3754 ( $\lambda$ 2664), the portion of the spectrum between $1/\lambda$ 3886 ( $\lambda$ 2573) and $1/\lambda$ 4113 ( $\lambda$ 2431) being almost entirely cut out. Beyond $1/\lambda$ 4415 ( $\lambda$ 2265) only one line at $1/\lambda$ 4545 ( $\lambda$ 2200) is visible.
0.625 per cent. ....	Spectrum continuous to $1/\lambda$ 4415 ( $\lambda$ 2265), but still somewhat weak beyond $1/\lambda$ 3896 ( $\lambda$ 2567). Complete absorption beyond $1/\lambda$ 4415 ( $\lambda$ 2265), except for feeble line at $1/\lambda$ 4545 ( $\lambda$ 2200).
0.312 per cent. ...	Spectrum continuous to $1/\lambda$ 4415 ( $\lambda$ 2265) and stronger than the preceding. A few lines showing faintly beyond.

(2) *Ammonium Chloride prepared by the neutralisation of ordinary Ammonia.*

Thickness of layer of solution in each case = 150 mm.

Strength of solution.	Description of spectrum.
2.5 per cent. ....	Spectrum continuous to $1/\lambda$ 3638 ( $\lambda$ 2748). <b>Absorption Band</b> $1/\lambda$ 3638— $1/\lambda$ 4243 ( $\lambda$ 2748— $\lambda$ 2356). Lines showing feebly at $1/\lambda$ 3694 ( $\lambda$ 2707), $1/\lambda$ 4112 ( $\lambda$ 2431), and $1/\lambda$ 4125 ( $\lambda$ 2424). Feeble spectrum beyond $1/\lambda$ 4243 ( $\lambda$ 2356).
1.25 per cent. ....	Spectrum almost continuous to $1/\lambda$ 4555 ( $\lambda$ 2195), but weak between $1/\lambda$ 3638 ( $\lambda$ 2748) and $1/\lambda$ 3886 ( $\lambda$ 2573); very weak between $1/\lambda$ 3886 ( $\lambda$ 2573) and $1/\lambda$ 4112 ( $\lambda$ 2431). Weak beyond.
0.625 per cent. ...	Spectrum continuous to $1/\lambda$ 4555 ( $\lambda$ 2195), with line showing beyond at $1/\lambda$ 4655 ( $\lambda$ 2148). Spectrum still weak between $1/\lambda$ 3886 ( $\lambda$ 2573) and $1/\lambda$ 4112 ( $\lambda$ 2431).

\* It may be noticed that the hydrochloric acid has apparently less absorptive power than water, which, of course, is impossible. The difference in the length of the spectra is owing to the greater sensitiveness for the extreme ultra-violet rays of the photographic plates which happened to have been used for the acid.



(3) *Pure Ammonium Chloride prepared from Ammonium Oxalate.*

Strength of solution.	Description of spectrum.
2.5 per cent. ....	<p>Spectrum continuous to <math>1/\lambda</math> 4556 (<math>\lambda</math> 2195), but weak beyond <math>1/\lambda</math> 4422 (<math>\lambda</math> 2261). Complete absorption beyond <math>1/\lambda</math> 4422 (<math>\lambda</math> 2261) except for line showing faintly at <math>1/\lambda</math> 4656 (<math>\lambda</math> 2148).</p> <p>The spectrum here is practically complete, and photographs of weaker solutions show little or no difference.</p>

(4) *Ammonium Chloride prepared by the reduction of Hydroxylamine.*

Solution containing 2.5 grams ammonium chloride in 100 c.c.

Spectrum continuous to  $1/\lambda$  4411 ( $\lambda$  2267), but weak from  $1/\lambda$  3886 ( $\lambda$  2573). No indication of selective absorption.

(5) *Pure Ammonium Chloride mixed with Pyridine.*

Solution containing 2.5 grams ammonia and 0.0001 gram pyridine in 100 c.c.

Spectrum continuous to  $1/\lambda$  3521 ( $\lambda$  2840). Complete absorption beyond.

Solution containing 2.5 grams ammonia and 0.00001 gram pyridine in 100 c.c.

Spectrum continuous to  $1/\lambda$  3638 ( $\lambda$  2749). Absorption Band from  $1/\lambda$  3638 ( $\lambda$  2749) to  $1/\lambda$  4306 ( $\lambda$  2322). Weak prolongation of spectrum to  $1/\lambda$  4555 ( $\lambda$  2195)

(6) *Pyridine Hydrochloride in Distilled Water.*

Solution containing 0.0001 gram pyridine in 100 c.c.

Spectrum continuous to  $1/\lambda$  3568 ( $\lambda$  2803). Complete absorption beyond.

Solution containing 0.00001 gram pyridine in 100 c.c.

Spectrum continuous to  $1/\lambda$  3638 ( $\lambda$  2749). Absorption Band from  $1/\lambda$  3638 ( $\lambda$  2749) to  $1/\lambda$  4306 ( $\lambda$  2322). Weak prolongation of spectrum to  $1/\lambda$  4555 ( $\lambda$  2195).

(7) *Methylamine Hydrochloride.*

Solution containing 2.5 grams methylamine in 100 c.c. water.

Spectrum practically the same as No. 3 (pure ammonia), with the weakening towards the end of the violet somewhat more pronounced.

(8) *Hydroxylamine Hydrochloride.*

Solution containing 2.5 grams hydroxylamine in 100 c.c. water.

Thickness of layer of solution = 150 mm.

Spectrum continuous to  $1/\lambda$  4413 ( $\lambda$  2266), but very weak from  $1/\lambda$  3886 ( $\lambda$  2573).

(9)

*Acetaldoxime.*

1.25 grams acetaldoxime in 100 c.c. water.

Thickness of layer of solution = 150 mm.

Spectrum continuous to  $1/\lambda$  3323 ( $\lambda$  3009). Complete absorption beyond.

1 mill.-mol. in 20 c.c. water.

Thickness of layer.	Description of spectrum.
mm.	
25	Spectrum continuous to $1/\lambda$ 3952 ( $\lambda$ 2530). Lines showing very faintly at $1/\lambda$ 4003 ( $\lambda$ 2498) and $1/\lambda$ 4023 ( $\lambda$ 2486). Complete absorption beyond.
20	Spectrum continuous to $1/\lambda$ 4034 ( $\lambda$ 2479). Complete absorption beyond.
15	Same as 20 mm., but portion of spectrum between $1/\lambda$ 3921 ( $\lambda$ 2550) and $1/\lambda$ 4034 ( $\lambda$ 2479) somewhat stronger.
10	Same as 15 mm., with very faint indication of prolongation to $1/\lambda$ 4125 ( $\lambda$ 2424).
5	Spectrum continuous to $1/\lambda$ 4125 ( $\lambda$ 2424) with faint indication of prolongation to $1/\lambda$ 4176 ( $\lambda$ 2394). Complete absorption beyond.
4	Spectrum continuous to $1/\lambda$ 4176 ( $\lambda$ 2394). Complete absorption beyond.
3	Spectrum continuous to $1/\lambda$ 4176 ( $\lambda$ 2394). Lines showing at $1/\lambda$ 4224 ( $\lambda$ 2367), $1/\lambda$ 4246 ( $\lambda$ 2355), and $1/\lambda$ 4321 ( $\lambda$ 2314). Complete absorption beyond.
2	Spectrum continuous to $1/\lambda$ 4321 ( $\lambda$ 2314). Line showing at $1/\lambda$ 4368 ( $\lambda$ 2289) and $1/\lambda$ 4417 ( $\lambda$ 2264). Complete absorption beyond.
1	Same as 2 mm., but somewhat stronger. With further dilution the extreme end of the ultra-violet appears. There is no indication of selective absorption.

(10)

*Ketoxime.*

1 mill.-mol. in 20 c.c. water.

Thickness of layer.	Description of spectrum.
mm.	
25	Spectrum continuous to $1/\lambda$ 3886 ( $\lambda$ 2573). Complete absorption beyond.
20	Spectrum continuous to $1/\lambda$ 3900 ( $\lambda$ 2564). Complete absorption beyond, except faint indication of line at $1/\lambda$ 3924 ( $\lambda$ 2548).
15	Same as 20 mm., but slightly stronger.
10	Spectrum continuous to $1/\lambda$ 3924 ( $\lambda$ 2548). Complete absorption beyond.
5	Same as 10 mm., with faint indications of lines at $1/\lambda$ 3963 ( $\lambda$ 2523) and $1/\lambda$ 4002 ( $\lambda$ 2499).
4	Spectrum continuous to $1/\lambda$ 4039 ( $\lambda$ 2476).
3	Same as 4 mm., but stronger.
2	Spectrum continuous to $1/\lambda$ 4039 ( $\lambda$ 2476), with lines showing at $1/\lambda$ 4115 ( $\lambda$ 2430) and $1/\lambda$ 4125 ( $\lambda$ 2424).
1	Spectrum continuous to $1/\lambda$ 4125 ( $\lambda$ 2424).

*Ketoxime*—(continued).

1 mill.-mol. in 100 c.c.

Strength of solution.	Description of spectrum,
mm.	
4	Spectrum continuous to $1/\lambda$ 4176 ( $\lambda$ 2394). Complete absorption beyond, except for lines at $1/\lambda$ 4245 ( $\lambda$ 2356) and $1/\lambda$ 4321 ( $\lambda$ 2314).
3	Spectrum continuous to $1/\lambda$ 4176 ( $\lambda$ 2394), with faint prolongation to $1/\lambda$ 4414 ( $\lambda$ 2265).
2	Spectrum continuous to $1/\lambda$ 4414 ( $\lambda$ 2265); with lines at $1/\lambda$ 4540 ( $\lambda$ 2203) and $1/\lambda$ 4555 ( $\lambda$ 2195).

We have to express our indebtedness to Mr. Alex. Lauder, of the University College of North Wales, Bangor, for the very valuable assistance which he has rendered us in carrying out a great part of this investigation.

XXX.—*Ammonium Amidosulphite*.

By EDWARD DIVERS and MASATAKA OGAWA.

THE interaction of such familiar gases as ammonia and sulphur dioxide ceased, sixty years ago and more, to attract the attention of investigators, notwithstanding comparatively nothing had then been definitely made out as to the nature of the product, even the few statements concerning it which occur in some of the best treatises on chemistry having but little experimental foundation. The history of the subject is briefly given on p. 331.

*Dry Sulphur Dioxide and Ammonia.*

Although sulphur dioxide and ammonia, even when comparatively well dried, unite at once and with great energy, yet if sufficient care has been taken to exclude moisture they do not combine. It has not been necessary, however, in order to demonstrate this striking phenomenon, to have resort to the elaborate precautions adopted by Brereton Baker in his well known experiments upon the non-union of hydrogen chloride and ammonia (Trans., 1894, 65, 611; 1898, 73, 422). As sulphur dioxide could be dried better than ammonia, using commercial phosphorus pentoxide for the purpose, we were successful in mixing the gases without their combining only on passing the dioxide first.

The preparation flask, with its tubes, having been heated and then kept for a time in the desiccator, was placed in ice and salt, and a slow current of sulphur dioxide sent through it, the gas having been dried by passing it first through tubes of sulphuric acid and then of phosphorus pentoxide. The outlet-tube dipped into mercury. Ammonia, dried first by cooling in a freezing mixture and then by passing it through long tubes of freshly fused and crushed potassium hydroxide (but no Stas's mixture) was now also passed into the flask slowly. The result was that the interior of the flask remained clear for some minutes, the mixed gases only combining on their escape through the mercury into the air with the production of white fumes of ammonium pyrosulphite; but after a time, the ammonia having, it is presumed, gradually brought in moisture along with it, through passing more rapidly along the tubes than at first, the walls of the flask became suddenly coated with an orange-coloured deposit, whilst the mercury rose high in the exit tube.

*Proportions in which Sulphur Dioxide and Ammonia Combine.*

The proportions in which ammonia and sulphur dioxide combine, or appear to combine, depend largely on the extent to which the temperature is allowed to rise, the heat of union being considerable. They vary also according as one or other of the gases is in excess, unless the temperature is kept very low. But variation in the proportions, as well as apparent condensation of additional sulphur dioxide by a sufficiently ammoniated product, is clearly due to secondary changes (p. 330). If the temperature is kept low, ammonia unites with sulphur dioxide, especially if the ammonia is in excess, in the proportion of two volumes of the former to one of the latter (p. 330), but since, at the ordinary temperature, this union is immediately followed by a decomposition in which ammonia is evolved, the union of the two gases may appear to take place in other proportions than those just mentioned. It is pretty certain that, by proceeding slowly enough and using strong cooling agents, secondary action can be almost entirely prevented, and the statement just made be verified even when working with the gases alone. We have not striven to make a very close approximation to such a result, because a simple modification of the method enabled us to exclude all secondary action. Our experimental work, which is referred to further on (p. 332), has shown that much more nearly two volumes than one volume of ammonia can be made in this way to unite with one volume of sulphur dioxide, the only proportions which Rose met with in his experiments (p. 332); and that the presence of much ammonium amidosulphite in the product can be established with certainty.

*Preparation and Analysis of Ammonium Amidosulphite.*

In order to get the primary product of the union of sulphur dioxide with ammonia in an unchanged state, ether was made use of. The ether, freed from alcohol and water by treatment with sodium, was contained in a small flask, fitted with inlet and outlet tubes, which was to serve, not only for the production of the new substance, but for its isolation and its weighing for analysis. The flask was put in a bath of ice and salt, with the outlet tube dipping into a trough of mercury, and the ether was saturated with dried ammonia; having shut off the ammonia, a very slow current of sulphur dioxide was then sent into the solution while the flask was continuously shaken, not only in order to diffuse the heat, but to prevent the product from caking on to the bottom of the flask and enclosing ether. The mouth of the tube containing the sulphur dioxide soon became filled with a yellow, pasty mass (p. 330), and had to be kept open by a platinum rod, manipulated through the rubber tubing above, but the precipitate itself was quite white and powdery. In spite of the external cooling, the heat of combining was sufficient to cause ammonia gas, saturated with ether vapour, to escape through the mercury sealing the exit tube, and when this escape became slight, the passage of sulphur dioxide was stopped. Using about 20 c.c. of ether, more than a gram of the substance was obtained. In order to secure this undecomposed, a second flask was put in connection with the preparation flask, and ammonia again passed to the saturation point. The ammoniated ether was decanted off through the connecting tube into the second flask, which was then detached, and the ether adhering to the precipitate was removed by passing a current of ammonia over the precipitate in the flask for some hours, the whole operation being carried out in the freezing mixture. There was no other means of completely drying the salt, and even this was not altogether successful if the salt had been allowed to cake together. Neither air nor hydrogen could be used in place of ammonia for drying the salt, nor could the flask remain out of the freezing mixture so long as ether still moistened the salt, without the latter acquiring an orange colour. When dry and in an ammoniacal atmosphere, the salt is more stable, but cannot long be kept at the ordinary temperature without becoming discoloured through decomposition.

*Analysis.*—The stopper carrying the gas tubes having been replaced by a plain one, and air allowed to displace most of the ammonia gas, the flask was at once weighed and left for a time inverted with the open mouth dipping into 100 c.c., or more, of water in a beaker. When the salt in it had become damp, it was washed into the water, and its very dilute solution distilled with alkali to determine the ammonia.

The residue was divided into two measured portions, one of which was acidified and heated at  $150^{\circ}$  under pressure for some hours, and then redistilled with alkali for additional ammonia, of which only a trace was obtained (0.001 per cent. of the salt). The other part of the solution was treated with bromine, and next with hydrochloric acid and potassium chlorate, after which the sulphuric acid was precipitated as barium sulphate with the usual precautions. The results of the analysis were :

	Ammonia.	Sulphur dioxide.
Found .....	35.09 ;	64.91 per cent.
$\text{SO}_2(\text{NH}_4)_2$ requires	34.69 ;	65.31 „

The slight excess of ammonia indicated may safely be attributed to the means taken to preserve the salt until it was analysed.

*Its Properties, Constitution, and Name.*

The new salt, which is white and apparently crystalline, seems to be slightly volatile in a current of ammonia. It is very deliquescent, and, on exposure to the air, decomposes, losing ammonia. It dissolves in water, giving out heat and a hissing sound, and if dissolved by ice or enough ice-cold water, furnishes a solution answering all the tests for pure ammonium sulphite. In this respect, it is quite unlike ammonium amidosulphate or carbamate, since even the latter salt gives at first no precipitate with calcium chloride, which at once precipitates all sulphite from the new salt. When the salt is much decomposed, its solution gives other reactions besides those of a sulphite. In anhydrous alcohol, it dissolves freely, evidently as ethyl ammoniumsulphite; it is also slightly soluble in dry ether. It soon begins to change, and then assumes an orange colour, even at the common temperature. At  $30$ — $35^{\circ}$ , it decomposes into a liquid and a solid part, both more or less orange-coloured, and into ammonia, the liquid part undergoing further change into solid matters (p. 333).

*Constitution.*—The salt is more probably an amido- than an imido-compound,  $\text{NH}_4 \cdot \text{N}(\text{SO}_2 \cdot \text{NH}_4)_2$  (analogue of normal ammonium imidosulphate), because it can be obtained only when the temperature is kept low and the ammonia is in excess. It is still more probably a sulphuryl rather than a thionyl compound, because of its feeble activity as a reducing agent, and of its very easy passage into ammonium sulphite or ethyl ammoniumsulphite. It has accordingly to be formulated as  $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{NH}_4$ , and not as  $\text{NH}_2 \cdot \text{SO} \cdot \text{ONH}_4$ .

*Name.*—Since the salt represents ammonium sulphite,  $\text{NH}_4 \text{O} \cdot \text{SO}_2 \cdot \text{NH}_4$ , in which the ammonoxyl is replaced by amidogen, it is properly called ammonium amidosulphite. Berglund's name of amidosulphonate, now in use for amidosulphate, is evidently based on a misconception.

The name, amidosulphinate, in analogy with amidosulphonate, must be rejected on the same grounds, and because the salt has not the characteristic reducing action and the constitution of sulphinates. It does not seem possible, even were it desirable, to construct a term for the first amide of sulphurous acid that would correspond with sulphamic acid, the synonym of amidosulphuric acid.

*Nature of the Decomposition which the Amidosulphite undergoes when Heated.*

*History.*—Experiments on the union of sulphur dioxide with ammonia made earlier than ours gave the products of decomposition of ammonium amidosulphite instead of the salt itself. Döbereiner, in 1826 (*Schw. Jahrb.*, 17, 120), described the product of the union as a brownish-yellow vapour which quickly condenses to a bright brown, solid mass, 'anhydrous ammonium sulphite,' which the smallest quantity of water converts into ammonium sulphite. Rose published three papers on "anhydrous sulphite of ammonia" in 1834, 1837, and 1844 (*Pogg. Ann.*, 33, 235; 42, 415; 61, 397), in the second correcting statements made in the first, and modifying, in the third, the views he had expressed in the earlier papers. The outcome was that he had ascertained that the product of the union is always one and the same single substance, in whatever proportions the dry gases are taken; that it is composed of equal volumes of the gases, is either yellowish-red and viscid, or red and crystalline, very deliquescent, and dissolves very easily in water without evolving ammonia; that it yields a neutral solution, which is at first yellowish, but soon becomes colourless, and gives, when recently prepared, the reactions mainly of a mixture of ammonium sulphate and trithionate, but to a small extent those of a sulphite also; and, lastly, that when the solution is of a certain concentration it gives a transient, reddish coloration with hydrochloric acid.

Forchhammer (*Compt. rend.*, 1837, 5, 395) found that, besides the orange-coloured substance, crystals of ammonium sulphate are produced, which can sometimes be seen apart from the other product in some spots of the mass, although often indistinguishably mixed up with it. (That the crystals observed in the product were those of sulphate could only have been a supposition of Forchhammer's.) The mass, when moistened, is alkaline, and evolves ammonia, yielding, in other respects, the reactions recorded by Rose. Absolute alcohol extracts from it a substance which acquires a rose colour, soon disappearing. Indirectly, he represented the mass to be derived from 2 mols. of ammonia to 1 mol. of sulphur dioxide.

The views advanced as to the nature of the orange-coloured sub-

stance have been, that it is a compound of ammonia with an isomeride of sulphurous anhydride, which, with water, changes at once into ammonium sulphate and trithionate, just as ammonium pyrosulphite slowly changes in hot solution (Rose); that it is amidogen sulphide,  $S(NH_2)_2$ , mixed with ammonium sulphate (Forchhammer); that it is partly thionamic acid,  $NH_2 \cdot SO \cdot OH$ , partly ammonium thionamate, both volatile, its colour being due to an impurity (H. Watts); and that it is ammonium pyrothionamate,  $NH_2 \cdot S_2O_4 \cdot NH_4$  (Jörgenssen).

*Interaction of the Gases.*—We have repeated Rose's experiments of measuring over mercury the volumes of the gases which interact, he having found that combination always takes place between equal volumes, whichever gas is in excess. The results somewhat approached this when no steps were taken to prevent the rise in temperature due to the union of the gases; but when the gas tube was immersed in a cooling mixture and the ammonia was in excess, the volume of this gas consumed was much greater than that of the sulphur dioxide. This method of investigating the matter is, however, inapplicable, because the ammonium amidosulphite which is formed partly decomposes and evolves ammonia freely. By letting the dried gases come together in a vessel agitated in a freezing mixture, and keeping the ammonia in excess, a solid mass is obtained which consists largely of the amidosulphite, and behaves as such with water, although it is mixed with other substances, quantitative analysis showing that much more than 3 mols. of ammonia to 2 mols. of sulphur dioxide are required for its formation. If, instead of being examined at once, it is kept for a long time in a gentle current of dry nitrogen or hydrogen at a temperature of  $30-35^\circ$ , it no longer contains amidosulphite or gives any sulphite to water, and contains not much more than one atom of nitrogen to one of sulphur. Thus, Rose's results are explained, and, at the same time, shown to be of no direct significance.

*Products of the Decomposition.*—Both Rose and Forchhammer found ammonium sulphate to be a principal constituent of the product of the interaction of the gases. If the temperature had risen sufficiently high, this would have been the case; furthermore, the solution of the even less heated product slowly becomes acid and full of sulphate. When, however, the temperature has not been allowed to exceed  $30^\circ$ , or even  $40^\circ$ , the quantity of sulphate in the product is so small that it may almost be disregarded. Together with the sulphate, trithionate was considered by Rose to make up most of the product, for the aqueous solution of the mass always gives a strong reaction with silver nitrate which might be that of trithionate; moreover, in the case of his product, other reactions of a trithionate were noticed. When, however, the product has been carefully prepared and is free from amidosulphite, its solution gives the silver reaction without the others which belong to a



trithionate. For instance, the solution may be acidified and left for hours without yielding more than mere traces of sulphur dioxide and sulphur; to get these in quantity, the solution has to be strongly heated under pressure. Besides this, the absence of sulphate in the solution is of itself almost enough to disprove the production of trithionate, since, as Rose himself held, sulphate and trithionate as products of the decomposition are complementary.

Pure ammonium amidosulphite, when heated, gives the same results as the coloured product obtained by the union of sulphur dioxide and ammonia.

Rose's assertion that the product formed by the union of the gases is homogeneous is certainly incorrect, according to our experience. By the union of the gases in a receiver kept well cooled, the product is deposited as a soft, waxy, yellow coating on the walls of the vessel and on the gas-tubes. Its colour varies in different parts from nearly white to orange-red, somewhat irregularly, but generally so as to be whiter near where the ammonia enters, the whiteness not being due to moisture in the gases, as Rose assumed. When the temperature rises to 30—35°, whether by the heat of reaction or by external heat, it is decomposed into an indistinctly crystalline, white solid, and a much smaller quantity of a coloured, effervescing liquid, partly draining to the bottom of the vessel; after a time, however, the whole becomes solid again, and adheres tenaciously to the glass. When pure ammonium amidosulphite is similarly heated in a dry, inactive gas, it becomes coloured, softens, sinters together, vesiculates, gives off ammonia, and becomes a mass like that derived directly from the union of the gases. With very gradual heating, the temporarily liquid product is much less coloured than in the other case, its colour being evidently caused by the presence of a red matter dissolved in it, which gives indications of being volatile.

This orange-red substance is never formed except in very small quantity. It gives a yellow colour to the aqueous solution of the whole product, which, however, slowly fades. Alcohol, carbon disulphide, and other menstrua dissolve it out from the salts, leaving them white; but the solutions are not pure. The yellow solution in water or alcohol takes a transient pink colour when mixed with dilute hydrochloric acid, and the alcoholic solution, an indigo-blue colour with concentrated ammonia. The residue left on evaporating the carbon disulphide solution becomes explosive when heated above 150°, and may then have become nitrogen sulphide, but before being heated it is not this substance.

Except the very little sulphate already mentioned, there is no known substance present in the residue of the decomposition of the amidosulphite by a gentle heat, so far as we can discover. Alcohol of

95 per cent. dissolves out something, but only very sparingly; on evaporating the solution in a vacuum, a very deliquescent salt is obtained in crystals, having a composition which may be expressed by  $9\text{NH}_3 \cdot 8\text{SO}_2$ , assuming the presence of 2.5 per cent. moisture. The composition of the whole crude residue does not differ much from this. The alcoholic solution, if cooled and saturated with ammonia, gives minute, scaly crystals in small quantity. This substance, dried in a current of ammonia, has a composition expressed by the formula  $(\text{NH}_3)_3\text{S}_2\text{O}_3$ , and if dried over sulphuric acid, that of  $(\text{NH}_3)_2\text{S}_2\text{O}_3$ . These three substances all give the silver nitrate reaction of the aqueous solution of the whole residue, and when boiled with dilute hydrochloric acid give very little sulphur and no sulphur dioxide. At higher temperatures, whether dry or in solution, they yield sulphur, sulphur dioxide, and sulphate. Two potassium derivatives of these salts have also been prepared. Neither the crude residue nor any of the above substances yields all its nitrogen as ammonia when distilled with alkali, unless it has been previously heated with hydrochloric acid under pressure.

From the mother liquor of the above-mentioned  $\text{S}_2\text{O}_3$  salt, a substance was obtained which in composition and behaviour appeared to be sulphamide, slightly impure. Neither sulphamide nor amidosulphate can be found in the fresh aqueous solution of the whole residue, but, by heating the solid residue itself to a higher temperature, imidosulphate is obtained in considerable quantity, besides sulphur and sulphate, and imidosulphate is known to be a product formed when either amidosulphate or sulphamide is first heated, and then dissolved in water. An extract from the residue made with proof-spirit or with wood spirit yields ammonium amidosulphate on evaporation, no doubt generated by hydration. When an aqueous solution of the heated residue was treated with excess of barium acetate, filtered, and evaporated at  $100^\circ$ , it left crystals of barium thiosulphate.

During the heating of ammonium amidosulphite at a temperature of  $30^\circ$  to  $35^\circ$ , besides much ammonia, small quantities of water and of sulphur dioxide are evolved, the former mainly in the earlier stage and the latter in the later stage of the decomposition. This remarkable production of water, although always evident, was fully established by cooling the escaping gases and testing the water thus collected. The presence of sulphur dioxide later in the operation was shown by the gases fuming on their escape into the air, and then forming a small, white deposit, slowly turning orange, and reacting as ammonium pyrosulphite. In the interaction of sulphur dioxide with ammonia, and in the decomposition of the amidosulphite, no liberation of nitrogen could ever be discovered.

To sum up the results of our incomplete work on the decomposition

of ammonium amidosulphite by a graduated and gentle heat: ammonia and a residue consisting of a substance (or substances) which behaves as a thio-amido-sulphonic compound are the principal products; in far smaller quantities, water and an orange-red substance are also produced, and generally, if not always, a very little sulphate; whilst as secondary products, apparently sulphamide and certainly amidosulphate and thiosulphate are obtainable, as well as imidosulphate, sulphur, and much sulphate. It seems of interest to point out that we here record the first production known of amidosulphate from ammonia and sulphur dioxide, this, hitherto, having been derived either from ammonia and sulphur trioxide, or from a nitrite and sulphur dioxide.

We hope in a future paper to be able to report the completion of this investigation.

### XXXI.—*Products of Heating Ammonium Sulphites, Thiosulphate, and Trithionate.*

By EDWARD DIVERS and MASATAKA OGAWA.

WHAT has been published on the effects of heating ammonium sulphites and thiosulphate is but little in accordance with the results of the experiments we have made on these salts and on the trithionate, in connection with an investigation of the decomposition which ammonium amidosulphite undergoes when heated.

#### *Preparation of the Salts used.*

*Ammonium Sulphite*,  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ .—Statements are conflicting as to whether this salt can be obtained from its solution by evaporation (Muspratt, *Phil. Mag.*, 1847, iii, 30, 414; Marignac, *Ann. Mines*, 1857, 12, 28; Ferriand, *Compt. rend.*, 1885, 100, 245; Hartog, *Compt. rend.*, 1887, 104, 1793; Röhrig, *J. pr. Chem.*, 1888, 37, 227). We find that a concentrated solution, charged with ammonia, will deposit the salt on evaporation over potash at the ordinary temperature, but in preparing this solution the moderately strong solution of ammonia, which must be used, has to be kept very cold while passing in the sulphur dioxide. If dilute, the solution does not yield the salt on evaporation, the greater portion of it being decomposed. Instead of evaporating, it is far better to take advantage of the sparing solubility of the salt in presence of much ammonia. Ammonia solution, sp. gr. 0.895, containing therefore about 28 grams ammonia in 100 c.c., is treated with sulphur dioxide, while the flask containing it is kept in

motion in a mixture of ice and salt, the tube conveying the sulphur dioxide not dipping into the solution. The formation of a very little orange-coloured matter in the neck of the flask cannot be avoided, but this can be easily removed afterwards. When the solution has become pasty from deposition of crystals of the salt, the passing of sulphur dioxide is stopped. Even at the common temperature, the crystals do not sensibly dissolve in presence of the excess of ammonia. The salt, drained on a tile under close cover, can be dried either by filter paper or by a short exposure in the desiccator over potassium hydroxide or carbonate, salted just before with ammonium chloride so as to maintain an atmosphere charged with ammonia. The product is equivalent in quantity to about one-fourth of the ammonia taken. By long exposure in a dried atmosphere, the salt becomes anhydrous without loss of ammonia. Exposed to the air, it deliquesces, owing to the fact that it evolves ammonia and becomes converted into the very deliquescent pyrosulphite.

*Anhydrous ammonium sulphite* is readily obtained from the hydrated salt by long enough exposure in the desiccator; it is very hygroscopic.

*Ammonium Pyrosulphite*,  $(\text{NH}_4)_2\text{S}_2\text{O}_5$ .—If, in the process described above, the passage of sulphur dioxide is not stopped when the solution is full of crystals, these gradually dissolve, and the solution becomes greenish-yellow. Then, as it gets saturated with sulphur dioxide in the cooling mixture, the pyrosulphite crystallises out, in quantity equivalent to a little more than one-fifth of the ammonia taken, being thrown out of solution by the sulphur dioxide. The salt can be obtained dry and pure in the same way as the normal sulphite, except that sulphuric acid, to which a little solid alkali sulphite has been added, is used in the desiccator. It may be kept unchanged for any time in such a desiccator, although it is very deliquescent and changeable when not carefully preserved from moisture. This salt is also easily obtainable by evaporating its aqueous solution, but not without some decomposition through loss of sulphur dioxide and through oxidation with formation of sulphate. It is much more soluble than the normal sulphite.

*Ammonium Thiosulphate*.—An old solution of calcium thiosulphate, obtained by boiling lime and sulphur together in water, and leaving the solution until much of the pentasulphide had been oxidised by the air, was decanted from insoluble matters, mixed with ammonium carbonate in excess, filtered, and then freely exposed to the air for some time at 50–60°. In this way, a very concentrated solution of ammonium thiosulphate was obtained, free from sulphate and other salts. The solution of this very soluble salt was then dried up to a crystalline mass in the desiccator. The well-dried crystals have been found by Fock and Klüss (*Ber.*, 1899, 32, 3099) to be anhydrous.

*Ammonium Trithionate*.—This salt does not appear to have been prepared hitherto. Being exceedingly soluble in water, it cannot be obtained by Plessy's excellent method for the potassium salt (*Ann. Chem. Phys.*, 1844, [iii], 11, 182), or by Hertlein's modification (*Zeit. physikal. Chem.*, 1896, 19, 287). We therefore made the pure potassium salt by Plessy's method, precipitated the potassium from it by hydrofluosilicic acid, neutralised quickly with ammonia, precipitated the ammonium trithionate by absolute alcohol, and dried it in the desiccator. This very deliquescent and changeable salt cannot be kept long in good condition, but it was used by us when freshly prepared and while still almost free from sulphate.

### *Effects of Heating the Salts.*

*The Process*.—The salts were heated in an oil-bath, in a subliming vessel consisting of a test-tube 15 cm. long and about 15 mm. in internal diameter. The tube was closed by a perforated caoutchouc stopper, a very slow current of dried nitrogen being passed through the tube and maintained during the heating and cooling. The salt, usually about 4 grams, was contained in an open, slender bottle, about 6 cm. long, having a platinum wire attached to it for lowering it into and lifting it out of the subliming tube. The tube was immersed in the oil to the level of the mouth of the bottle inside, so as to cause all dry sublimates to collect in the tube above this level. When, as in the case of the hydrated normal sulphite, the heating was divided into stages, the bottle was transferred between these to a second subliming tube. The heating of the oil was conducted very slowly, so that the temperatures mentioned, which were those of the oil, may be accepted as being very nearly those of the salts at the time.

In describing the effects of heating them, the salts are taken in the inverse order in which their preparation was described, this being more convenient on account of the nature of the products.

*Ammonium Trithionate*.—This salt is scarcely affected until the temperature is above 150°, and at 160–170° it steadily decomposes into sulphur dioxide and a residue of ammonium sulphate and unfused sulphur. It is remarkable that the sulphur does not fuse, and this can only be referred to the presence of minute quantities of impurities. It all dissolved readily in carbon disulphide, and crystallised out on evaporating the solvent.

It can hardly be doubted but that *ammonium tetrathionate* (and *pentathionate*, if it can exist) would decompose in the same way as trithionate. *Ammonium hyposulphate* (*dithionate*) has been shown by Heeren (*Ann. Phys. Chem.*, 1826, 7, 55), and more definitely by Klüss (*Annalen*, 1888, 246, 194) to first become anhydrous, when heated, and then

to decompose at about  $130^{\circ}$  into sulphur dioxide and ammonium sulphate.

*Ammonium Thiosulphate.*—Rammelsberg (*Pogg. Ann.*, 1842, 56, 298), found that this salt, when heated, gave water, ammonia, and a sublimate of sulphur, much thiosulphate again and sulphite, and a little sulphate. This result must have been obtained by rough heating. A much more weighty statement is that made by Spring (*Ber.*, 1874, 7, 1159), namely, that the dry salt can be sublimed unchanged, intermediate dissociation being admitted. We have found it to decompose very slowly at  $150^{\circ}$ , the main products being a sublimate of anhydrous normal sulphite and a residue of unfused sulphur, as in the case of the trithionate. Very small quantities of hydrogen sulphide and ammonia also passed off in the current of nitrogen, and the sublimate contained a very little of a salt which had some of the properties of trithionate, and did not give the violet coloration with ferric chloride characteristic of a thiosulphate. Analyses of the sublimate, and of that part of the salt which remained mixed with the sulphur when the progress of the decomposition was arrested after about half of it had been decomposed, gave results showing that the former is essentially anhydrous normal sulphite, and the latter unchanged thiosulphate:

	Ammonia.	Sulphur.
$(\text{NH}_4)_2\text{SO}_3$ .....	29.31 per cent.	27.59 per cent.
Sublimate.....	27.54     "	27.55     "
$(\text{NH}_4)_2\text{S}_2\text{O}_3$ .....	22.97     "	43.24     "
Residue.....	20.69     "	42.31     "

The main decomposition of the thiosulphate is in full agreement with the relation of thiosulphates to sulphites. Very interesting is the production of a little ammonia and hydrogen sulphide, in connection with the relation of trithionate to thiosulphate as its thio-anhydride (Spring):  $2(\text{NH}_4)_2\text{S}_2\text{O}_3 = 2\text{NH}_3 + \text{SH}_2 + (\text{NH}_4)_2\text{S}_3\text{O}_6$ . When ammonium thiosulphate is rapidly and more strongly heated, ammonia is lost, and sulphur sublimes; then, as a matter of course, and of no significance, thiosulphate and even trithionate are produced on adding water to the mixed sublimate.

*Ammonium Pyrosulphite.*—We could not get this exceedingly deliquescent salt into the tube ready for heating before it had absorbed some moisture, and to this we attribute some of the results obtained. Change went on slowly in the salt at  $130^{\circ}$ , and somewhat faster at  $150^{\circ}$ . At first, there was little else than a slight, but steady, evolution of sulphur dioxide, and this continued, although very feebly, to the end, and while the sublimate was forming. The sublimate was pyrosulphite, in one experiment, and in another, this salt mixed with a very little anhydrous sulphite. There was, however, a considerable

residue, amounting to more than one-third of the weight of the salt taken, and consisting of sulphate, trithionate, sulphur, and apparently some tetrathionate. There was neither sulphite nor thiosulphate. The tetrathionate, the sulphur, and the sulphur dioxide were very probably derived from decomposition of trithionate by moisture. From a consideration of the results, it seems almost necessary to assume that perfectly dry pyrosulphite sublimes unchanged (with no doubt intermediate dissociation), and that the presence of a little moisture causes it to decompose partly into sulphate and trithionate.

*Anhydrous ammonium sulphite* volatilises at about  $150^{\circ}$ , yielding a sublimate of the same salt, or rather a pseudosublimite, for the salt surely dissociates when heated.

*Hydrated Ammonium Sulphite*.—According to Muspratt, this salt volatilises entirely when heated, no sulphate being produced; it yields water, then much ammonia, and finally a sublimate which, judging from its properties, is ammonium pyrosulphite. We observed the following effects on gradually heating it in a very slow current of dried nitrogen. At about  $90^{\circ}$ , the salt became moist and ammonia escaped; at a little above  $100^{\circ}$ , distillation of water also took place, both water and ammonia continuing to escape in noticeable quantities for  $2\frac{1}{2}$  hours longer, when the temperature for some time had been  $120^{\circ}$ ; up to this, but very little sublimate had formed, and matters were now almost at a standstill. The quantity of the salt heated was about 4 grams, and this had now lost one-fifth of its weight, the residue having the composition expressed by the formula  $(\text{NH}_3)_{10}(\text{SO}_2)_6(\text{H}_2\text{O})_7$ , equivalent to a mixture or combination of the three salts, hydrated sulphite (39.4 per cent.), anhydrous sulphite (34.1 per cent.), and pyrosulphite (26.5 per cent.), dividing equally amongst them the sulphur dioxide. Repetitions of the experiment gave practically the same results. Calculation and the results of one experiment gave the following numbers:—

	Ammonia.	Sulphur dioxide.
$(\text{NH}_3)_{10}(\text{SO}_2)_6(\text{H}_2\text{O})_7$ .....	25.00 per cent. ;	56.47 per cent.
Found .....	24.65     ,,	56.20     ,,

If, in the formation of this complex, which no longer loses material quantities of ammonia or water, only these products had been given off, the residue should have been  $84\frac{1}{2}$  per cent. of the hydrated normal sulphite, whereas it proved to be little more than 79 per cent., in consequence of the volatilisation of some of the (dissociated) salt, rendered manifest by the production of a little sublimate.

After renewing the heating in a fresh subliming tube, allowing the temperature to rise slowly from  $120^{\circ}$  to  $150^{\circ}$ , the residue had almost all disappeared in 2 hours, an abundant dry sublimate being deposited; for some time during the heating, sulphur dioxide escaped

steadily, but practically ceased to do so long before the sublimation was finished. The residue left when sulphur dioxide ceased to come off proved, on analysis, to be normal sulphite, but only half hydrated,  $2(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ . The sublimate, also, now and at the finish, consisted of normal sulphite, apparently anhydrous, although, as it is very hygroscopic, it was found to be a little hydrated from unavoidable exposure to the air while it was being scraped out of the tube into the weighing bottle.

Hydrated ammonium sulphite, therefore, when gradually heated to  $120^\circ$ , becomes converted one-third into the anhydrous salt, and one-third into pyrosulphite, by loss of water and ammonia; and then the nearly stable complex of these salts, with the other third of the original salt, becomes converted into the nearly anhydrous normal sulphite between  $120^\circ$  and  $150^\circ$ , sulphur dioxide and water escaping. The presence of water is essential to the occurrence of both changes; dry ammonium pyrosulphite partly sublimes as such at  $150^\circ$ , and partly changes into sulphate and trithionate, as already described. If heated more rapidly in an open tube, the results will be those obtained by Muspratt, for then water is more quickly expelled, and some pyrosulphite can be deposited as a sublimate.

### XXXII.—*The Combination of Sulphur Dioxide and Oxygen.*

By EDWARD JOHN RUSSELL and NORMAN SMITH.

In the course of a number of analyses involving the separation of sulphur dioxide and oxygen by means of a pellet of manganese dioxide, it was noticed that the amount of gas absorbed was always greater than the amount of sulphur dioxide present, some of the oxygen being taken up and sulphuric acid formed. Part only of the sulphur dioxide was absorbed in accordance with the equation  $\text{SO}_2 + \text{MnO}_2 = \text{MnSO}_4$ , the rest combined with oxygen in a manner that suggested surface action on the part of the manganese dioxide, thus:  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ . This apparent surface action occurring in the cold, was thought to be of sufficient importance to deserve further investigation, especially as up to the present sulphur dioxide and oxygen are only known to combine directly at high temperatures.

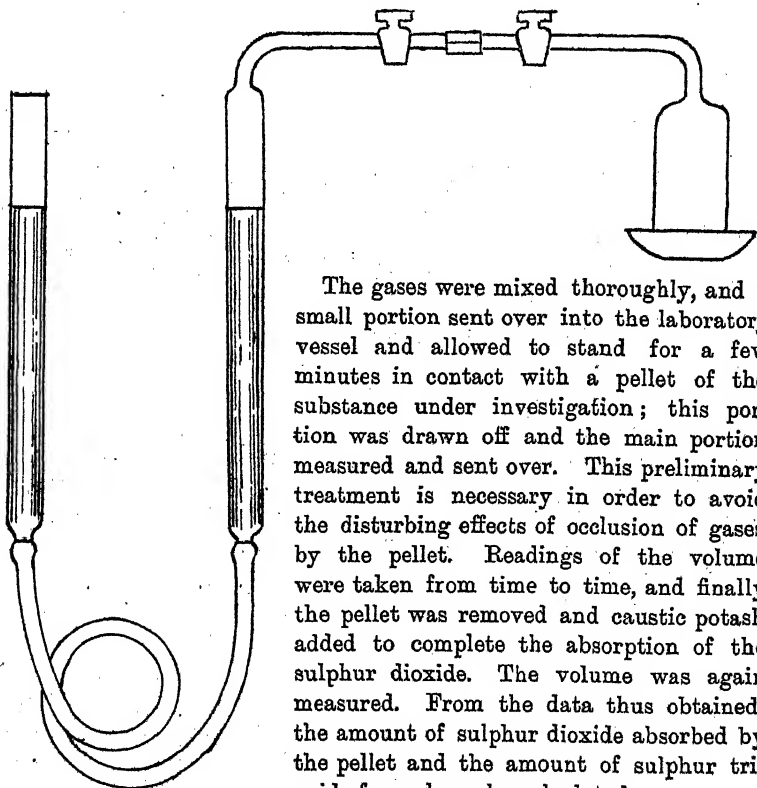
#### I. ACTION OF SULPHUR DIOXIDE ON OXYGEN IN PRESENCE OF MOIST OXIDES.

The apparatus consisted of a laboratory vessel and eudiometer connected together and filled with mercury. Air was introduced into the



eudiometer and its volume measured; sulphur dioxide, delivered from a syphon of the liquid, was bubbled into the laboratory vessel, transferred to the eudiometer, and its volume measured. By introducing the gases in this order, and never having too great an excess of sulphur dioxide, the deviation of this gas from Boyle's law became very slight.

FIG. 1.



The gases were mixed thoroughly, and a small portion sent over into the laboratory vessel and allowed to stand for a few minutes in contact with a pellet of the substance under investigation; this portion was drawn off and the main portion measured and sent over. This preliminary treatment is necessary in order to avoid the disturbing effects of occlusion of gases by the pellet. Readings of the volume were taken from time to time, and finally the pellet was removed and caustic potash added to complete the absorption of the sulphur dioxide. The volume was again measured. From the data thus obtained, the amount of sulphur dioxide absorbed by the pellet and the amount of sulphur trioxide formed can be calculated.

In order to show that the substance formed is sulphuric acid, the pellets of pyrolusite, after exposure to the mixed gases, were left for  $1\frac{1}{2}$  hours in a stream of dry carbon dioxide to remove any sulphur dioxide mechanically held, and then washed with water. Part of the washings was tested for sulphur dioxide with a strip of paper soaked in a potassium iodate and starch solution, and the rest with methyl-orange solution. Sulphur dioxide was found to be absent, and methyl-orange showed that the solution was strongly acid. Since manganese sulphate is neutral to this indicator, the acidity must be due to sulphuric acid.

It was next necessary to find out how much, if any, oxygen was taken up by the sulphur dioxide dissolved in the water present in the pellet, or by the potassium sulphite formed in the final operation. For this purpose, experiments were made as described above, but recourse was had to pellets of moistened silica instead of manganese dioxide, in order to match as far as possible the surface conditions under which the water acted. In no case did the absorption of oxygen exceed 1/15 of that observed in the experiments in which manganese dioxide was used. It is evident, therefore, that this absorption must be due to some action exercised by the manganese dioxide.

A series of experiments was next made with manganese dioxide in different states. We used the native oxide in experiments 1—14, and the precipitated oxide in experiments 15—18.

TABLE I.

No. of expt.	Vol. of air.	Vol. of $\text{SO}_2$	$\text{SO}_2$ absorbed (= $\text{MnSO}_4$ ).	$\text{SO}_2$ unchanged.	$\text{SO}_2$ con- verted into $\text{SO}_3$ .	Time of exposure.	Substance used.
1	93	100	56	39	5	40 mins.	Small pellet of pyrolusite.
2	93	"	60	30	10	40 "	Same sample, pellet double size.
3	107	"	47	47	6	60 "	Fresh sample, small pellet.
4	101	"	68	12	20	60 "	Same sample, pellet double size.
5	77	"	56	19	25	50 "	Pyrolusite, lump not moistened.
6	77	"	57	21	22	50 "	
7	60	"	91	2	7	10 "	Pyrolusite, powdered and made into pellet, moistened.
8	59	"	94	1	5	10 "	
9	94	"	67	26	7	6 1/2 hrs.	The same, after standing 18 hours in air at ordinary temperatures.
10	56	"	44	47	9	18 "	The same, after standing 4 days in air at ordinary temperatures.
11	83	"	70	4	26	48 "	The same, after standing 21 days in air at ordinary temperatures.
12	81	"	58	26	16	18 "	Pyrolusite, moistened and dried for 2 hours at 100°.
13	76	"	28	66	6	18 "	
14	66	"	47	42	11	48 "	Precipitated $\text{MnO}_2$ dried in air for 1 day.
15	78	"	84	1	15	15 mins.	
16	75	"	83	2	15	15 "	Precipitated $\text{MnO}_2$ dried in air for 12 days.
17	76	"	87	3	10	15 "	
18	80	"	91	2	7	15 "	

The pellets used were about the size of a large pea, except in experiments 2 and 4, in which they had, as nearly as we could judge, about twice the surface of the others.

The conclusions we draw from this series of experiments are :

1. The percentage of sulphur trioxide formed depends on the extent of surface of the pellet (experiments 1—4).

2. Ordinary pyrolusite only slowly absorbs sulphur dioxide, but forms a large percentage of sulphur trioxide (experiments 5 and 6).

3. If the pyrolusite is moistened, the rate of absorption of sulphur dioxide very much increases, but the percentage of sulphur trioxide formed diminishes (experiments 7 and 8).

4. As the moisture is removed, either by slow evaporation in the air or by more rapid evaporation at  $100^{\circ}$ , the rate of absorption of sulphur dioxide diminishes, and the percentage of sulphur trioxide formed increases.

5. The oxide obtained by precipitation produces less sulphur trioxide than the native compound. This is probably accounted for by the difference in surface.

A second series of experiments was made, using lead peroxide. The commercial precipitated oxide was digested with dilute nitric acid, well washed with water, and allowed to stand in the air for the periods specified below:

TABLE II.

No. of expt.	Vol. of air.	Vol. of $\text{SO}_2$ .	$\text{SO}_2$ absorbed (= $\text{PbSO}_4$ ).	$\text{SO}_2$ unchanged.	$\text{SO}_2$ con- verted into $\text{SO}_3$ .	Time of exposure.	Substance used.
1	75	100	97	3	nil	15 mins.	Lead peroxide, dried for 2 days in air at the ordinary temperature.
2	85	"	98	2	"	15 "	
3	77	"	98	2	"	15 "	
4	79	"	98	2	"	15 "	
5	86	"	92	3	5	20 "	Same sample, dried for 20 days in air.
6	72	"	91	3	6	20 "	
7	97	"	95	2	3	15 "	Last sample moistened.
8	87	"	95	2	3	15 "	

The conclusions to be drawn are :

1. Lead peroxide, when freshly washed, causes practically no combination of sulphur dioxide and oxygen, hence its suitability for determining sulphur dioxide in gas analysis.

2. After standing for some time in the air, it becomes capable of causing the union of sulphur dioxide and oxygen.

3. Samples which have once acquired this property do not lose it at once on moistening.

We have frequently noticed, during gas analysis, that unless the lead peroxide is freshly washed, there is always a disappearance of oxygen even after moistening. This is in agreement with the results of experiments 7 and 8.

A third series of experiments was now carried out, to find out how far this surface action was a general property of the metallic oxides.

TABLE III.

No. of expt.	Vol. of air.	Vol. of SO <sub>2</sub>	SO <sub>2</sub> absorbed by oxide.	SO <sub>2</sub> unchanged.	SO <sub>2</sub> converted into SO <sub>3</sub> .	Time of exposure.	Substance used.
1	67	100	39	51	10	18 hrs.	Chromium dioxide, CrO <sub>2</sub> .
2	77	"	88	12	nil	15 mins.	Barium dioxide, moistened and dried 18 hours in air.
3	92	"	100	nil	"	25 "	
4	81	"	93	7	"	40 "	
5	84	"	78	22	"	2 hrs.	*Stannic oxide washed with nitric acid.
6	94	"	85	15	"	45 mins.	Chromium trioxide, CrO <sub>3</sub> .
7	89	"	98	2	"	20 "	
8	124	"	90	10	"	15 "	
9	81	"	89	11	"	20 "	Barium hydroxide.
10	66	"	4	96	"	60 "	
11	57	"	5	95	"	60 "	Granular copper oxide.
12	95	"	96	4	"	2 hrs.	
13	90	"	94	6	"	25 mins.	Aluminium hydroxide dried at 100°.
14	82	"	55	31	14	30 "	
15	92	"	73	14	13	30 "	Chromium hydroxide dried at 100°.
16	82	"	74	20	6	40 "	
17	61	"	80	16	4	30 "	Ferric hydroxide dried at 100°.
18	73	"	81	19	nil	25 "	
19	73	"	70	27	3(?)	20 "	Same sample moistened.
20	83	"	41	50	9	3 hrs.	
21	77	"	51	36	13	25 mins.	Ferric oxide moistened.

\* On coming into contact with the sulphur dioxide, the stannic oxide became yellow in colour.

These results show :

1. That this surface action is exhibited only by the neutral peroxides MnO<sub>2</sub>, PbO<sub>2</sub>, and CrO<sub>2</sub>, and by ferric and chromic oxides and hydroxides.

2. This surface action is very different from the ordinary oxidation of sulphur dioxide and of sulphites. Water, caustic potash, barium and aluminium hydroxides, and copper and tin oxides have all been exposed to mixtures of sulphur dioxide and oxygen, but under the conditions of these experiments no oxygen was taken up, although quantities of sulphur dioxide were in each case absorbed.

All the oxides so far investigated have absorbed sulphur dioxide, but this absorption has not invariably been accompanied by the surface action.

The next point was to find out whether this surface action could take place in the cold, unaccompanied by any absorption of sulphur dioxide by the reagent used.

Hæmatite, platinised pumice, platinised asbestos, and finely-divided platinum (obtained by slow reduction by means of sodium formate acting in the cold) were all tried with negative results. In the last case, some absorption of sulphur dioxide occurred, due, no doubt, to moisture adhering to the platinum, but oxygen was not absorbed.

We must, then, conclude that when this surface action takes place, it is dependent on a simultaneous combination of the oxide used with sulphur dioxide, and, in fact, seems to proceed simultaneously with this combination.

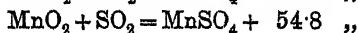
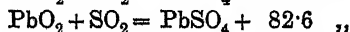
### *Discussion of the Results.*

In the case of chromic and ferric hydroxides, the action might of course be due to the formation of a sulphite with subsequent oxidation to sulphate, but it then becomes difficult to understand why the percentage of sulphur trioxide should be less in experiments 18 and 19 than in experiments 16 and 17 in Table III; one would rather expect it to be the converse.

We have sought for some reason why there should be more combination over manganese peroxide than over lead peroxide, and more over lead peroxide than over barium peroxide. These three were selected because there can be no doubt that the reactions are simply the two already given, namely :



Surface conditions may account for the different amounts of sulphur trioxide formed, but we would suggest that the heat evolved by the combination of the sulphur dioxide with the peroxide may exert a considerable influence. The thermal data are :



The second only is the result of direct experiment (Tscheltzow, *Compt. rend.*, 1885, 100, 1459), the others are calculated from the figures given in Berthelot's "Thermochimie" (1897).

It has long been suspected, and recently proved, that the condition most favourable for the formation of sulphur trioxide from sulphur dioxide and oxygen in presence of spongy platinum is that the heat of reaction shall be conducted away as rapidly as possible. In the cases before us, it will be noticed that barium and lead peroxides rapidly absorb sulphur dioxide (15 to 30 minutes only being required) and disengage large quantities of heat. This sudden development of a large quantity of heat is not favourable to the formation of sulphur trioxide. Manganese peroxide, on the other hand, if fairly dry, only

slowly absorbs sulphur dioxide, and there is a smaller heat evolution; this slow dissipation of a smaller quantity of heat favours the production of sulphur trioxide. If, however, the peroxide is moistened, its combination with the sulphur dioxide becomes more rapid and the heat is more quickly liberated so that the conditions are rendered unfavourable, and the percentage of sulphur trioxide diminishes.

A mixture of sulphur dioxide and oxygen affords an instance of "false equilibrium." There is no appreciable amount of combination, but if combination occurred, energy would be dissipated. The necessary factors for this seem to be certain conditions of surface and the constant addition of a limited supply of energy. Our experiments are interesting as showing that the latter can be supplied in the form of chemical energy from a simultaneous reaction, and need not be supplied in the form of heat.

## II. EXPERIMENTS WITH DRIED SUBSTANCES.

Having found that the combination of manganese peroxide with sulphur dioxide ceases when moisture is absent, we proceeded to further test our conclusion that the formation of sulphur trioxide is dependent on a simultaneous combination of the peroxide with sulphur dioxide, by repeating some of the experiments given in Table I with carefully dried substances, and found that the surface action also ceased, there being no absorption whatever.

The manganese dioxide was prepared by two methods:

(a) Ignition of carefully recrystallised manganese nitrate, the temperature being raised by slow stages during 7 days to  $120^{\circ}$ , and finally kept for 6 hours at  $155^{\circ}$ .

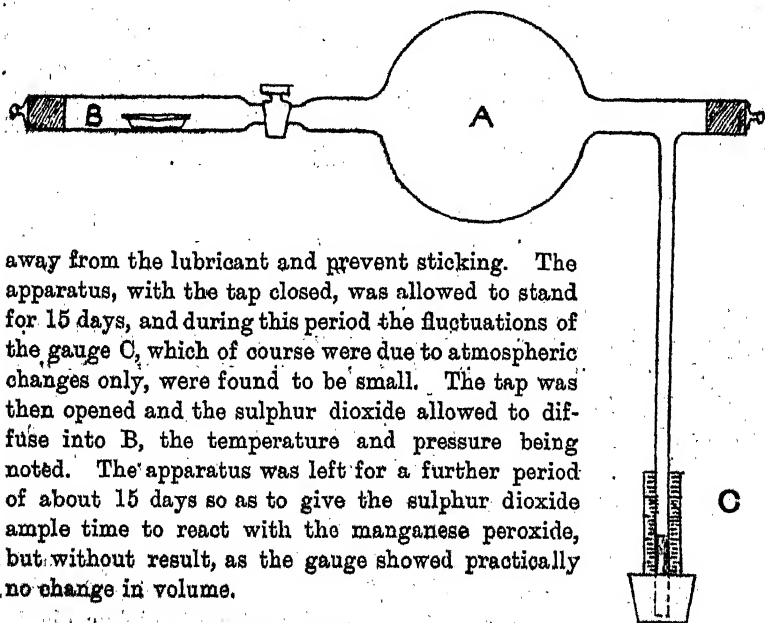
(b) Precipitation by Volhard's method, manganese sulphate, nitric acid, and potassium permanganate being allowed to react under the conditions given in Wright and Menke's paper (Trans., 1880, 37, 22). The precipitated oxide was digested with nitric acid, washed by decantation, collected by the aid of the pump, and dried at  $100^{\circ}$ . In order to exclude dust during filtration, the funnel containing the substance was closed by a glass plate through which a hole had been drilled. A tube, fitting tightly through this, delivered air purified by passing through a long column of sulphuric acid.

The oxides thus obtained were placed in porcelain boats and kept sealed up in exhausted tubes with phosphorus pentoxide. After standing in a warm place for two or three weeks, they were introduced into the experimental tubes.

The sulphur dioxide was prepared by heating a concentrated solution of potassium hydrogen sulphite. A very steady stream of the gas is thus obtained and is easily kept under control.

The apparatus, shown in figure 2, was constructed from glass tubing which had been carefully washed with fuming nitric acid to remove dust and grease; after completion, it was again washed and then dried by heating in a large flame and passing a current of dry air. The bulb, A, contained sulphur dioxide standing over distilled phosphorus pentoxide, whilst B was filled with nitrogen and contained the manganese dioxide and more phosphorus pentoxide. The tap and stoppers were lubricated with deliquesced phosphorus pentoxide, and coated on the outside with a mixture of beeswax and vaseline to keep moisture

FIG. 2.



away from the lubricant and prevent sticking. The apparatus, with the tap closed, was allowed to stand for 15 days, and during this period the fluctuations of the gauge C, which of course were due to atmospheric changes only, were found to be small. The tap was then opened and the sulphur dioxide allowed to diffuse into B, the temperature and pressure being noted. The apparatus was left for a further period of about 15 days so as to give the sulphur dioxide ample time to react with the manganese peroxide, but without result, as the gauge showed practically no change in volume.

(1).—May 19, apparatus filled.

June 1, tap opened. Bar. 766.2 mm., temp. 19.4°, gauge 13 mm.

„ 13, „ „ 764.6 „ „ 19.6° „ 9 „

Eliminating the effect due to the change in atmospheric conditions, we find that, as a matter of fact, there is a slight increase in volume.

(2).—May 19, apparatus filled.

June 1, tap opened. Bar. 766.2 mm., temp. 19.4°, gauge 16.5 mm.

„ 13, „ „ 764.6 „ „ 19.6° „ 12.0 „

Here again the increase is slightly greater than it should have been.

(3).—June 3, apparatus filled.

June 16, tap opened. Bar. 762.2 mm., temp. 20.2°, gauge 1.0 mm.

„ 26, „ „ 765.6 „ „ 17.9° „ 0.0 „

In experiments 1 and 2, the oxide used was prepared by ignition; in experiment 3 by precipitation. In no case was any diminution in volume noticed. The apparatus would readily indicate any diminution, as a preliminary experiment had shown that when the materials were not dried the mercury in the gauge rapidly rose, on one occasion to the extent of 450 mm. in one hour.

Having shown that dry manganese peroxide is without action on dry sulphur dioxide, we proceeded to examine the effect of exposing dried mixtures of sulphur dioxide and oxygen to the dried peroxide and found that in no case did any diminution in volume occur, consequently no interaction took place. The same apparatus was used, but the bulb A was filled with a mixture of sulphur dioxide and oxygen whilst B contained oxygen instead of nitrogen.

(4).—June 13, apparatus filled.

June 26, tap opened. Bar. 765.7 mm., temp. 18.2°, gauge 11 mm.

July 4, „ „ 763.2 „ „ 18.0° „ 12 „

(5).—June 13, apparatus filled.

June 26, tap opened. Bar. 765.7 mm., temp. 18.2°, gauge 10 mm.

July 4, „ „ 763.2 „ „ 18.0° „ 9.5 „

(6).—July 4, apparatus filled.

July 15, tap opened. Bar. 763.4 mm., temp. 19.6°, gauge 21 mm.

„ 21, „ „ 761.8 „ „ 20.4° „ 19 „

The conclusion cannot be drawn that the formation of sulphur trioxide has ceased because the combination of manganese peroxide and sulphur dioxide has also ceased, for it may happen that when the materials are pure, "contact action," even with the addition of energy, is no longer effective in producing combination of sulphur dioxide and oxygen. This point was tested in the next series of experiments.

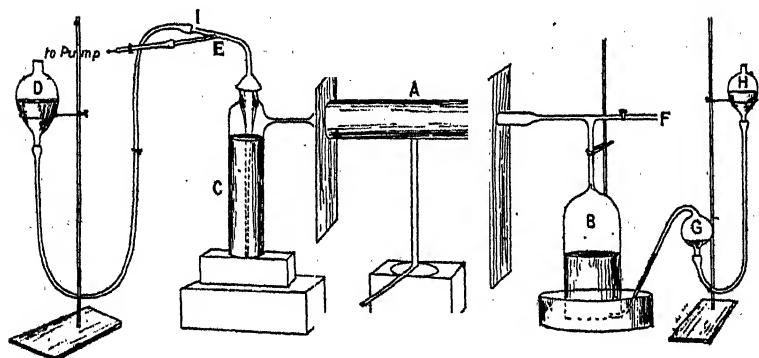
### III. COMBINATION OF SULPHUR DIOXIDE AND OXYGEN IN PRESENCE OF HEATED PLATINUM.

This reaction affords a very good instance of the point we wished to investigate. In ordinary circumstances, the contact action of the platinum, aided by the energy continuously supplied from the source of heat, brings about combination. Our object was to discover whether this would still be the case when care was taken to dry and purify all the materials. The apparatus used is shown in Fig. 3.



The glass tube, A, contains platinised pumice, and is heated by means of a Ramsay burner to 400—450°. It is sheathed with a copper jacket and provided with asbestos screens to protect the rest of the apparatus from the heat. One end is fused on to the glass vessel B, which contains oxygen standing over mercury. B also contains a quantity of phosphorus pentoxide scattered about so as to coat the surface of the glass and mercury. The other end of A is fused on the vessel C, also of glass, filled with mercury and connected by flexible tubing with the reservoir D. C also contains phosphorus pentoxide covering the walls and the ground-in tube running from I to the bottom of C. In case any air should leak in between the glass and the india-rubber tubing at I, a T-piece was inserted at E and connected with a pump. Any leakage could be at once detected and the air pumped out. The phosphorus pentoxide used was distilled in oxygen, and the mercury sent several times through a Meyer's purifying apparatus.

FIG. 3.



The sulphur dioxide stood over mercury and phosphorus pentoxide in the bulb G provided with a tube dipping under the mercury into reservoir B. It was kept under diminished pressure, the mercury always standing several inches high in the delivery tube. The vessel H contained mercury, and by unscrewing the clamp the sulphur dioxide could be driven out into B.

The platinised pumice was prepared as follows: platinum black was dissolved in aqua regia, and the solution evaporated to dryness on the water-bath, taken up with water, and filtered. Pumice broken into small pieces was boiled for 45 minutes with aqua regia, well washed with water, and dried over the Bunsen burner. It was soaked in the platinum solution, then in ammonium chloride solution, dried at 130°, and ignited over the blow-pipe in a clay crucible for 2 hours. When not in use, it was kept in exhausted tubes with phosphorus pentoxide. A sample of this platinum, tested in the apparatus before drying,

showed a copious production of sulphur trioxide when sulphur dioxide and oxygen were passed over it.

There were three stages in the experiment :

*1st Stage. Drying the Platinised Pumice and the Apparatus.*—B was clamped firmly in position, A rested on supports, and C stood on smooth blocks, which were well oiled so as to allow a certain amount of movement as A expanded on heating.

After A had been heated for some hours, the reservoir D was lowered, drawing the mercury out of C, and causing some oxygen to pass from B over the pumice to C. Any moisture brought away from A would be absorbed by the phosphorus pentoxide in C. The oxygen was then driven back into B, and this operation was repeated for one hundred times at intervals of one or two hours during the working day. This stage occupied about three weeks.

*2nd Stage. Introduction of the Sulphur Dioxide. The Reaction in the Dry State.*—While the platinum and oxygen were being dried, the sulphur dioxide was drying in the bulb G. F was now connected with the pump and some of the oxygen withdrawn from B; mercury was run from H into G, and the displaced sulphur dioxide entered B, the total volume being marked. After an hour's diffusion, the mixed gases were passed backwards and forwards over the platinum. In none of the three experiments carried out could any white fumes be seen, but this does not imply that no sulphur trioxide was formed, because there were probably very few particles of dust or aqueous vapour to act as "nuclei of condensation," Aitken having shown that in the absence of these, fumes may sometimes not make an appearance. The proof that sulphur trioxide was not formed lay in the fact that there was no diminution in volume. To find out whether combination had altogether stopped, or had only been retarded, we prolonged this stage in one experiment for 5 hours, but no concentration was observed.

*3rd Stage. Introduction of Steam. The Reaction in the Moist State.*—The tap F was connected with a vessel containing steam, and opened for an instant while some of the steam was drawn into A. White fumes instantly appeared and a considerable diminution in volume was observed. In one experiment, in which a large quantity of phosphorus pentoxide was present, this diminution fell off after a short time, but on introducing more water vapour a further diminution in volume was observed.

The details of one experiment are given, the results in the case of two others being similar :

Volume of oxygen about .....	250 c.c.
" sulphur dioxide .....	65 "
Mixed gases passed backwards and forward over pumice in A.	
After 5 hours. Contraction .....	Nil.

After introducing steam and again passing over pumice in A.		
1st passage (10 mins.).	Contraction .....	13 c.c.
2nd " ( $\frac{1}{2}$ hour).	" .....	3 "
After 24 hours.	" .....	29
More steam introduced and after further standing.	Contraction .....	27
		} "
Total contraction .....		56 "

In no case did combination entirely cease. Although no contraction could be observed after the dried gases had stood for 5 hours in contact with the heated platinum, yet an appreciable diminution was noticed when they had been in contact with it during 24 hours. It is, however, very difficult to dry platinised pumice completely, and our experiments, showing, as they do, the great influence of moisture on the velocity of the reaction, point to the conclusion that sulphur dioxide and oxygen will not combine in contact with heated platinum if moisture is carefully excluded.

### *Conclusions.*

(1) When a mixture of sulphur dioxide and oxygen is allowed to stand over certain metallic oxides at the ordinary temperature, combination takes place to a certain extent between the two gases, owing to the "surface action" exerted by the metallic oxide.

(2) With the same oxide, the amount of sulphur trioxide formed depends on the extent of the surface of the oxide.

(3) With the same oxide, this amount depends also on the state of the surface. It appears to be least with freshly precipitated oxides which are not yet dried, and to increase if the oxide has been moderately heated or kept for a long time so as to become dry.

(4) The amount appears to be absolutely dependent on a simultaneous combination of the oxide with sulphur dioxide, and in fact seems to proceed concurrently with this. Several cases have been observed in which sulphur dioxide was absorbed without any combination with oxygen, but no case could be discovered in which the two gases combined without a reaction taking place between the sulphur dioxide and the metallic oxide or other substance.

(5) The most striking instance of this surface action is afforded by manganese peroxide, some 20 per cent. of the sulphur dioxide being converted into sulphur trioxide. If the materials are carefully dried by means of phosphorus pentoxide, no combination takes place, as even after standing for several days no alteration in volume can be detected. By drying the mixture, combination of manganese dioxide and sulphur

dioxide is thus prevented, as is also the surface action of the oxide which brings about the union of sulphur dioxide and oxygen.

(6) When sulphur dioxide and oxygen are passed over heated platinised pumice, combination diminishes as the materials are more completely dried, and can be made very small. Hitherto it has been generally held that the "contact action" of platinum could bring about combination even in the absence of any impurity, but this does not appear to be the case in the present instance.

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### XXXIII.—*Notes on the Estimation of Gaseous Compounds of Sulphur.*

By EDWARD JOHN RUSSELL.

THERE are two chief difficulties attending the estimation of gases containing sulphur when only small quantities of the mixtures are available: one arises from the fact that, during explosion with oxygen, sulphur trioxide is invariably formed in addition to the dioxide; the other from the fact that, when absorption methods are used, other gases, and particularly oxygen, are absorbed. The first of these difficulties can be entirely overcome by introducing an equation allowing for the formation of sulphur trioxide; the second can, in certain cases, be partially obviated by modifying the conditions of absorption.

In this paper, an account is given of methods which have been found to work satisfactorily for the estimation of the four common gases containing sulphur, namely, sulphur dioxide, hydrogen sulphide, carbonyl sulphide, and carbon disulphide, when only one of them is present in the gas mixture. If two or more are present at the same time, the methods will not always work well.

#### I. SULPHUR DIOXIDE.

At the ordinary temperature and pressure, this gas does not obey Boyle's law, and hence volumetric methods are not available if its partial pressure is great. When, however, its partial pressure is less than one-third of the total pressure, good results can be obtained.

Sulphur dioxide being very soluble in water, all water in excess of that required to saturate the gases in the eudiometer must be removed. This is most conveniently effected by allowing the moistened eudio-

meter, filled with mercury, to stand for some time, and then running off the drops of water which accumulate at the top. The gaseous mixture can now be introduced.

*Absorption by Caustic Potash, Carbon Dioxide being absent.*—This method can be used in presence of oxygen when the amount of sulphur dioxide is not more than 20 per cent. of the whole volume, and the oxygen is well diluted with an inert gas. The following examples show the accuracy attained :

	Present.	Found.	Present.	Found.
SO <sub>2</sub> .. ...	13·03	12·89	20·00	19·98
O <sub>2</sub> .....	18·18	18·29	17·02	17·04
N <sub>2</sub> .....	68·78	68·80	62·98	62·98 (by diff.)

If larger quantities of sulphur dioxide are present, good results are not obtained. The solution used for absorption contains one part of caustic potash to two of water. Absorption is rapid and, after agitating two or three times, complete. Even when the gas remains in contact with the reagent for some time, there is no absorption of oxygen provided sufficient inert gas is present.

*Absorption by Lead or Manganese Peroxide.*—Berzelius and Marcet (*Phil. Trans.*, 1813, 103, 186) first used lead peroxide to separate sulphur dioxide from carbon dioxide, and found the separation to be quantitative and complete in one hour. Bunsen ("Gasometry," Eng. Edition, 1857, 84) recommends a bullet of manganese peroxide. Both act very well, but Norman Smith and I have found (this vol., p. 342) that, if oxygen is present, some of it combines with part of the sulphur dioxide to form sulphur trioxide owing to the surface action of the peroxide, and thus the dioxide comes out too high. Lead peroxide exerts much less surface action than the manganese compound, and is therefore to be preferred. By carefully observing the following details, the surface action can be reduced to a minimum, and under favourable circumstances is negligible.

Commercial lead peroxide, after digestion for some time with warm dilute nitric acid, is well washed with water and dried between folds of filter paper. A cake is thus formed from which small pieces are easily broken off; these constitute the "pellets" and act much better when obtained in this way than if prepared by heating the peroxide in a mould. It is essential that the peroxide should be used within a few days of this treatment. The pellet must be small and must be moistened with a drop of water, but it should remain quite firm and not be pasty. Absorption should be complete within five or

ten minutes; if it takes longer than this, the analysis should be rejected.

Another difficulty lies in the tendency of the pellet to occlude other gases within its pores. In order to overcome this difficulty, Bunsen recommends pouring syrupy phosphoric acid over the pellet, but this very much retards absorption, many hours or days often being necessary before it is complete. The same result can be attained without the use of phosphoric acid by sending over a small portion of the gas into the laboratory vessel and introducing the pellet; in a short time, equilibrium is set up between the pellet and the gas from which the sulphur dioxide is to be abstracted. This portion is now drawn off and the main portion sent over. In order to be certain that all the sulphur dioxide is removed from the eudiometer, the gases should be returned to the eudiometer and again passed into the laboratory vessel. The following experiments were made with lead peroxide :

	Present.	Found.	Present.	Found.
SO <sub>2</sub> .....	19.7	19.8	34.5	34.4
CO <sub>2</sub> .....	80.3	80.2	65.5	65.6
SO <sub>2</sub> .....	12.90	13.10	55.72	56.02
O <sub>2</sub> .....	37.75	37.75	9.27	8.94
N <sub>2</sub> .....	49.35	49.15	35.01	35.01

*Absorption by Chromic Acid Solution.*—This operation is carried out in a Hempel's pipette. 10 grams of chromium trioxide are dissolved in 150 c.c. of a saturated solution of calcium chloride and the whole introduced into the pipette. The gases are allowed to stand over it for 10 minutes, absorption being then complete. The calcium chloride is necessary in order to diminish the solubility of the carbon dioxide. The following results have been obtained :

	Present.	Found.	Present.	Found.
SO <sub>2</sub> .....	18.5	18.3	46.0	46.2
CO <sub>2</sub> .....	37.3	37.5	40.2	40.0

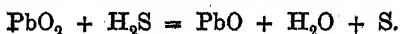
Of these three methods, absorption by lead peroxide is by far the best.

## II. HYDROGEN SULPHIDE.

The gas was generated by acting on ferrous sulphide with sulphuric acid, and was passed through water and through calcium chloride into

a bulb surrounded by solid carbon dioxide, where it very rapidly condensed to a clear and colourless liquid, any hydrogen present being thus removed. When several c.c. had collected, the bulb was removed, and the liquid allowed to volatilise. It was noticed that the earlier fractions of the gas caused the surface of mercury over which it was stored to become tarnished in a day or so, but that with later fractions, the surface remained bright for weeks. It appears then, that, contrary to the usual statement, pure hydrogen sulphide does not cause the surface of mercury to become blackened.

*Absorption by Lead Peroxide.*—Precipitated lead peroxide (washed with nitric acid), when not too dry, absorbs the gas very quickly,\* but cannot be used in presence of oxygen or of carbon dioxide, either of these being absorbed simultaneously with the hydrogen sulphide. The reaction, according to my results, is apparently :



The lead oxide thus formed readily absorbs carbon dioxide and hydrogen sulphide :

18.4 vols.  $\text{H}_2\text{S}$  and 33.6 vols.  $\text{CO}_2$  gave an absorption of 25.4 vols.  
 28.8 „  $\text{H}_2\text{S}$  „ 48 „  $\text{CO}_2$  „ „ 46.8 „

when lead peroxide was used. This absorption of carbon dioxide does not take place if the pellet is moistened with phosphoric acid, but, as already remarked, the absorption in any case becomes so slow that the method is totally inapplicable whenever time is any object,

Manganese peroxide behaves in a precisely similar manner.

*Absorption by Caustic Potash.*—Caustic potash, also, is not a useful absorbent for hydrogen sulphide, owing to the ease with which potassium sulphide takes up oxygen. If sufficient zinc sulphate has been added to the caustic potash, this absorption of oxygen is very much reduced, but the reagent cannot be relied upon to give very satisfactory results, as the following analyses made with it show :

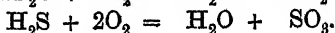
	Present.	Found.	Present.	Found.
$\text{H}_2\text{S}$ .....	27.2	28	27.7	27.7
$\text{O}_2$ .....	19.2	18.4	63	63
$\text{N}_2$ .....	72.6	72.6	—	—

The action of lead hydroxide suspended in potash is even less accurate.

*Estimation by Explosion with Air and Oxygen.*—This is the method

\* Apparently absorption is retarded when too much water is present.

most generally applicable. In the explosion, some sulphur trioxide is nearly always formed; we have therefore to deal with two reactions:



If  $x$  is the part burning to  $\text{H}_2\text{O}$  and  $\text{SO}_2$ ,  
 and  $y$  „ „ „  $\text{H}_2\text{O}$  „  $\text{SO}_3$ ,  
 Then the contraction =  $3x/2 + 3y$ ,  
 oxygen used =  $3/2x + 2y$ ,  
 and  $\text{SO}_2$  formed =  $x$ ,

$x$  and  $y$  can thus be found, and their sum gives the quantity of hydrogen sulphide present. If the mixture will not explode, carbon monoxide and oxygen may be added.

Mixtures of hydrogen sulphide and oxygen (diluted with air), on explosion, gave the following percentage results:

$\text{H}_2\text{S}$ present.....	4.57	8.02	9.8	14.6	18.67
$\text{H}_2\text{S}$ found.....	4.74	8.04	9.6	14.8	18.48

In the first three cases, explosion was brought about by adding carbon monoxide and oxygen.

Combustion proceeds quite smoothly when the gas is sufficiently diluted. There must, of course, be an excess of oxygen, and to every volume of explosive mixture there should be  $1\frac{1}{2}$ —2 volumes of inert gas. With a view to further testing the method, mixtures of hydrogen sulphide, carbon dioxide, oxygen and nitrogen were analysed:

	Present.	Found.	Present.	Found.
$\text{H}_2\text{S}$ .....	13.40	12.91	20.94	21.12
$\text{CO}_2$ .....	25.13	25.39	33.56	33.41
$\text{O}_2$ .....	32.82	33.28	23.56	23.37
$\text{N}_2$ .....	28.63	28.42	21.94	22.10

### III. CARBONYL SULPHIDE.

*Absorption by Alcoholic Potash.*—Alcoholic potash is usually quoted as the best absorbent, but is not of wide application since many gases, although not absorbed by caustic potash, are soluble to some extent in the alcohol present. Thus the method cannot be used for separating carbonyl sulphide from carbon monoxide. Again, as potassium sulphide is formed when carbonyl sulphide reacts with either aqueous or alcoholic potash, the method cannot be used in presence of oxygen, this being rapidly absorbed by alkali sulphides. If oxygen is absent,



a solution of 1 part of caustic potash in 4 parts of water absorbs the gas rapidly, and gives good results; addition of more potash retards absorption:

	Present.	Found.	Present.	Found.
COS .....	27·6	27·5	52·53	52·67
CO .....	72·4	—	47·47	47·33

In presence of oxygen, very fair results can be obtained by using a solution of 1 part of caustic potash in 4 of water, containing excess of freshly precipitated zinc hydroxide in suspension.

	Present.	Found.	Present.	Found.
COS .....	31	31·1	43·4	43·6
Air .....	81·8	—	198·6	—

Unless the oxygen is as much diluted as in air, some of it is always absorbed and the result is too high.

Other oxides (for example, lead oxide), suspended in caustic potash, potassium hypobromite, &c., do not act so well.

*Manganese peroxide* and *lead peroxide* do not absorb carbonyl sulphide, but in presence of moisture partial hydrolysis takes place with formation of carbon dioxide and hydrogen sulphide. Attempts to separate sulphur dioxide or hydrogen sulphide from carbonyl sulphide by means of these reagents did not usually give satisfactory results.

*Estimation by Explosion with Oxygen.*—This method is the one most generally applicable, being in fact the only one which can be used in presence of carbon dioxide.

When carbonyl sulphide is exploded with excess of oxygen in a long tube so that the explosion wave is set up, the products are of a complicated character, and contain carbon monoxide, unchanged carbonyl sulphide, and sulphur, as well as carbon dioxide, sulphur dioxide, and sulphur trioxide.

If, however, the explosion takes place in a eudiometer under diminished pressure, the only products are sulphur trioxide, sulphur dioxide, and carbon dioxide, unless the explosion is violent, in which case some sulphur escapes combustion and is deposited, and part of the nitrogen unavoidably present is oxidised. Whilst oxidation of the nitrogen and deposition of sulphur can be prevented by sufficiently diluting the explosive mixture with air, it has not been found

Let  $x$  be the part of the carbonyl sulphide burning to  $\text{CO}_2$  and  $\text{SO}_2$ ,  
and  $y$  " " " " " $\text{CO}_2$  "  $\text{SO}_3$ .

$$\begin{aligned} \text{Then contraction} &= x/2 + 2y, \\ \text{SO}_2 \text{ found after explosion} &= x. \end{aligned}$$

If oxygen is also present, its amount is found by adding to the oxygen left after explosion the amount required for combustion of the carbonyl sulphide (namely,  $\frac{3}{2}x + 2y$ ), and of any other combustible gases present, and subtracting from this total the amount of oxygen added.

Mixtures of carbonyl sulphide and oxygen, on explosion with air, gave respectively 11.79, 14.2, 26.9 per cent. of carbonyl sulphide, instead of 11.85, 14.5, 27.3 per cent.

Some more complex mixtures were made up and analysed:

	Present.	Found.	Present.	Found.
COS.....	9·6	9·7	18·16	18·48
CO <sub>2</sub> .....	16·2	16·0	13·42	12·77
SO <sub>2</sub> .....	—	—	8·71	8·78
CO .....	8·5	8·6	12·59	12·61
O <sub>2</sub> .....	44·4	44·1	10·88	10·82
N <sub>2</sub> .....	21·3	21·7	41·24	41·61

The nitrogen was estimated by difference, and the carbon monoxide

\* The analogy to the combustion products of carbon disulphide (Dixon and Russell, Trans. 1899, 75, 600) should be noted. Carbonyl sulphide further resembles carbon disulphide in that it undergoes phosphorescent combustion before actually igniting.

by absorption, in a separate sample which had been allowed to stand over caustic potash.

#### IV. CARBON DISULPHIDE.

The only useful absorbent for the vapour of this substance is alcoholic potash, and the application of this reagent in gas analysis, for reasons already stated, is very limited.

Explosion with oxygen gives good results. Dixon and Russell have found that in a short tube the products consist of carbon dioxide, sulphur dioxide, and sulphur trioxide. Applying the equations as in previous cases,

If  $x$  represents the part burning to  $\text{CO}_2$  and  $\text{SO}_2$   
 and  $y$  " " " "  $\text{CO}_2$  "  $\text{SO}_3$   
 then contraction  $= x + 4y$   
 $\text{SO}_2 = x/2$   
 Total  $\text{CS}_2 = x + y$ .

The results obtained by explosion are very accurate.

Pedler (Trans., 1890, 57, 625) attempted to estimate carbon disulphide by explosion with oxygen, and found his figures did not at all agree with those calculated from the equation:



He suggested that the discrepancy might be due to oxidation of nitrogen, and the resulting oxides combining with the sulphur dioxide and steam present to form lead chamber crystals, though he only seems to have experimentally shown a disappearance of nitrogen in two cases.

Fortunately, Pedler published all his analytical data, and I have calculated from these the composition of the mixture, using the equations given above. The agreement between the values found and the quantities originally taken show that his suggestion is probably wrong, and that his results are consistent with the equations given above.

The following table contains, in the first three columns, Pedler's experimental data, in the other three columns, my results calculated from them. The carbon dioxide and the carbon disulphide should be identical in volume; the difference represents Pedler's experimental error. The value of the method would, of course, be destroyed if it were necessary to make use of the carbon dioxide determination to calculate the amount of carbon disulphide present, but obviously a calculation of the amount of carbon disulphide from the sulphur dioxide alone gives results which are too low. The discrepancy becomes even greater when we bear in mind that Pedler estimated sulphur dioxide by means of a bullet of manganese peroxide, which

causes some sulphur dioxide to combine with part of the excess of oxygen, thus producing a greater decrease in volume than is accounted for by the amount of sulphur dioxide present. On the assumption that 6 per cent. of oxygen is absorbed (which represents a very fair average, see preceding paper), the columns marked "corrected" have been calculated; these, of course, are simply given as an indication, as there is no means of finding out what was the amount of oxygen actually absorbed.

CS <sub>2</sub> taken.	CO <sub>2</sub> found.	$\frac{1}{2}$ SO <sub>2</sub> found.	Corrected SO <sub>2</sub> .	CS <sub>2</sub> calculated.	Corrected CS <sub>2</sub> .
$\alpha$ { 6.27	6.83	6.23	5.88	6.45	6.19
6.26	6.28	5.79	5.44	6.34	6.08
4.97	4.77	4.68	4.38	4.94	4.72
4.82	4.67	4.4	4.2	4.72	4.57
$\beta$ { 4.50	4.48	4.17	3.92	4.59	4.41
4.67	4.56	4.4	4.2	4.70	4.55
5.70	5.85	5.42	5.12	5.96	5.73
4.22	4.09	3.91	3.66	4.25	4.07
$\gamma$ { 4.05	4.09	3.89	3.64	4.25	4.06
5.17	5.12	5.0	4.7	5.42	5.10
$\delta$ 4.18	4.22	3.99	3.75	4.38	4.12

Had Pedler used lead peroxide instead of manganese peroxide, the "corrected" columns would not have been necessary.

If we reject all cases where the experimental error was large, that is, where the numbers for the carbon disulphide taken and the carbon dioxide found do not nearly coincide, it will be seen that the values for the former come out fairly well.

Mixtures of several gases, each containing sulphur, cannot generally be analysed by explosion, unless the amounts of one or more of them are known. Each new gas introduces, of course, two new unknown quantities—its share of the sulphur dioxide and its share of the sulphur trioxide—and a sufficient number of equations may not be obtainable. For instance, mixtures of carbonyl sulphide, carbon disulphide, and carbon dioxide cannot be analysed by explosion. Absorption methods not being very reliable, no general scheme can be laid down for analysis, and each mixture must be treated as a special case.

Messrs. Norman Smith and Nicoll have made some of the analyses quoted in this paper, and I wish to tender to them my best thanks for their assistance.

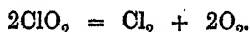
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### XXXIV.—*Influence of the Nascent State on the Combination of Dry Carbon Monoxide and Oxygen.*

By EDWARD JOHN RUSSELL.

So large a number of pairs of substances are known which require the presence of traces of a third substance before they will combine, that there does not seem much reason for adding to their number in the present state of our knowledge. It is, however, both of interest and of importance to find out how far the action of the third substance is modified when the conditions are varied; when, for example, high temperatures are introduced, or one of the pair of substances is in the nascent condition. Some experiments bearing on this form the subject of the present communication. The example chosen for investigation was the very well known one of carbon monoxide and oxygen.

Some time ago, it was shown by Professor Dixon and the author (*Trans.*, 1897, 71, 605) that when carefully dried mixtures of carbon monoxide with excess of chlorine peroxide were sparked, an explosion took place, but a large part of the carbon monoxide was not affected thereby, and the chief reaction was simply the ordinary explosive decomposition of chlorine peroxide, thus :



Although an excess of oxygen was present in the nascent condition and at a high temperature, it nevertheless failed to attack more than one-half to one-third of the carbon monoxide present.

The author has since studied several other reactions in which carbon monoxide and oxygen are brought together in the flame of an explosion, one of them being in the nascent condition.

It is not possible to completely separate the two factors nascent condition and high temperature, because the nascent state implies that a reaction is going on, and a reaction that proceeds with explosion develops a considerable amount of energy. The amount of energy developed can be varied, however, by varying the reaction, and, by keeping the nascent condition constant, some idea can be obtained of the relative influence of the two factors.

The substances used as sources of nascent oxygen were chlorine monoxide and chlorine peroxide; and, as sources of nascent carbon monoxide, carbonyl sulphide, and nickel carbonyl.

#### I. *Interaction of Oxygen and Nascent Carbon Monoxide.*

(a) *Combustion of Carbonyl Sulphide.*—Than showed in 1867 (*Annalen, Suppl.*, 5, 236) that when carbonyl sulphide is passed through a heated

tube, it decomposes into carbon monoxide and sulphur. Berthelot (*Compt. rend.*, 1878, 87, 573) mentions a second decomposition represented by the equation:



but the only evidence he gives is based on thermal considerations, which show that such a reaction would proceed with development of heat. It is true that if carbonyl sulphide, as ordinarily prepared, is passed through a glass tube heated to redness, much carbon disulphide is present in the escaping gases, but I find that if the carbonyl sulphide is previously purified by passing either through triethylphosphine or over wood charcoal, no carbon disulphide can be detected in the products of decomposition.\* In these experiments, the temperature was varied from about 200° to a bright red heat, and the main reaction was found to be expressed by the equation:



For the purpose of these experiments, the carbonyl sulphide was prepared by Klason's method (*J. pr. Chem.*, 1887, [ii], 36, 64). A mixture of 290 c.c. of concentrated sulphuric acid with 400 c.c. of water was cooled, 50 c.c. of a solution of potassium thiocyanate saturated at the ordinary temperature were added, and the whole heated to 25° on the water-bath. Carbonyl sulphide is slowly evolved without any frothing taking place, and can be collected and stored over sulphuric acid. The impurities invariably present are carbon dioxide, carbon disulphide, and hydrogen sulphide; hydrogen cyanide is absent if pure potassium thiocyanate is used in the preparation.

The carbon disulphide was removed by ignited wood charcoal, the carbon dioxide by caustic potash,† and the hydrogen sulphide either by means of mercuric oxide or by long standing over sulphuric acid.

When the gas so prepared is mixed with excess of oxygen (2 volumes) in a eudiometer and sparked, a violent explosion takes place and the products are carbon dioxide, sulphur dioxide, sulphur trioxide, and some sulphur.

If the removal of hydrogen sulphide has been made more complete by leaving the gas for 2—3 days in contact with dry mercuric oxide (over mercury), and if the mixture with oxygen is dried for several days over phosphorus pentoxide, an explosion still takes place on sparking, but it is much less violent, and combustion is in no case complete. Even in presence of the *excess* of oxygen, much sulphur is deposited, and carbon monoxide remains unburnt; in fact, when the

\* Hoesvay (*Bull. Soc. Chim.*, 1882, [ii], 37, 294) showed that wood charcoal entirely removes carbon disulphide from carbonyl sulphide.

† A strong solution of caustic potash only slowly absorbs carbonyl sulphide, dilute solutions, however, act rapidly.

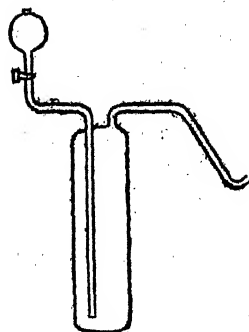
gas is transferred to another eudiometer and caustic potash added to absorb the products of combustion and any unchanged carbonyl sulphide, a residue of gas is left which explodes violently on sparking.

Analysis showed that, of the original carbonyl sulphide,

about 50—60 per cent.	was burnt,
„ 10	„ „ unchanged,
„ 30—40	„ „ converted into CO.

The purification was next carried a step further by leaving the gas for 3 weeks in contact with pure sulphuric acid instead of treating it with mercuric oxide. The gasholder used is shown in Fig. 1, and was made by sealing a tap funnel on to a glass wash bottle of 200 c.c. capacity.

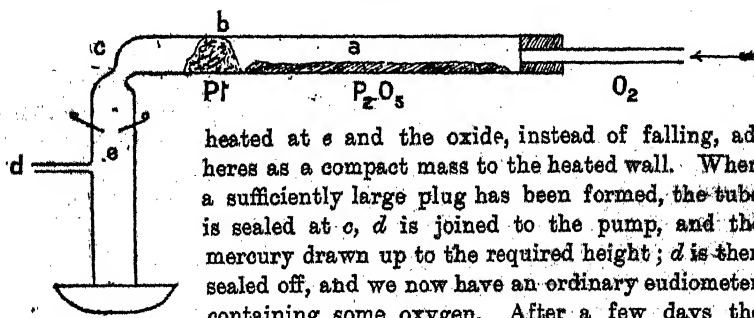
FIG. 1.



The phosphorus pentoxide was carefully distilled in a stream of oxygen over red hot, spongy platinum as recommended by Shennstone and Beck (*Trans.*, 1893, 63, 475), and, in order to avoid contact with air, was distilled directly into the eudiometers, which were constructed as shown in Fig. 2.

Phosphorus pentoxide, introduced into the part *a*, is slowly volatilised, and carried by the stream of oxygen over red hot, spongy platinum at *b* to the cooler part of the tube, where it condenses to a snowy mass and falls on to the surface of the mercury without adhering to the walls. The first portion can thus be rejected. The tube is now

FIG. 2.



heated at *e* and the oxide, instead of falling, adheres as a compact mass to the heated wall. When a sufficiently large plug has been formed, the tube is sealed at *c*, *d* is joined to the pump, and the mercury drawn up to the required height; *d* is then sealed off, and we now have an ordinary eudiometer containing some oxygen. After a few days the requisite amount of carbonyl sulphide is introduced by breaking the end of the delivery tube of the gasholder under the mercury and running a measured volume of sulphuric acid into the holder. The mixture was then allowed to dry for three weeks.

In some experiments, the carbonyl sulphide was left for some days

over ignited and purified charcoal before treatment with sulphuric acid, and the mercury used in the eudiometer was distilled in a vacuum.

On sparking these mixtures, explosions usually took place, but in one case the flame died out about half-way down the tube, and in another there was no explosion. The general result obtained on analysing the products showed that

25—40	per cent.	was burnt.
25—35	„	unchanged.
30—40	„	converted into CO.

It follows from these experiments that, as the quantity of impurity diminishes,

- (1) the amount of carbonyl sulphide unburnt increases,
- (2) the amount of carbon monoxide produced and left unburnt increases.

The first of these conclusions indicates that pure carbonyl sulphide will not burn when sparked with oxygen; this point will be further dealt with later. The second gives us the very interesting result that to a great extent carbon monoxide is not attacked by oxygen even when it is freshly produced in the flame of an explosion in presence of an excess, and sometimes a large excess, of oxygen.

In this reaction, there is probably very little heat developed on the whole. Thermal data as given by different observers vary greatly, but it would appear that the splitting up of carbonyl sulphide into carbon monoxide and sulphur requires addition of energy, and this would use up the heat derived from the combustion which does take place.

I now proceeded to study the effect of increasing the energy of the reaction by exploding mixtures of carbonyl sulphide, carbon disulphide, and oxygen. These were made by adding known quantities of the gaseous mixture,  $\text{CS}_2 + 3\text{O}_2$ , to measured volumes of carbonyl sulphide with excess of oxygen. The effect of even a small addition of carbon disulphide is to diminish greatly the amount of carbon monoxide left unburnt. With 4 per cent. of carbon disulphide in the mixture, 9 per cent. of carbon monoxide was found unburnt.

The energy was now increased in a different way, namely, by liberating carbon monoxide by the explosion of nickel carbonyl and oxygen—a reaction known to proceed with great development of heat.

(b) *Combustion of Nickel Carbonyl*.—Nickel carbonyl readily reacts with oxygen in the cold, sometimes with violent explosion.\* The

\* On one occasion, some nickel carbonyl, when introduced into a eudiometer containing oxygen over mercury, caused so violent an explosion that the eudiometer was shattered, and two of us standing near were badly cut.

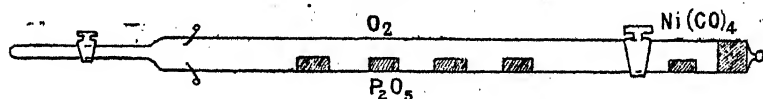


experiment was therefore carried out in a eudiometer with two chambers so that the two substances could be dried separately (Fig. 3). The nickel carbonyl was contained in a glass boat. After standing for a few days, the tap was turned so that the vapour of the carbonyl could diffuse into the oxygen; after an hour, the tap was closed and an electric spark was passed, producing an explosion. Analysis showed that some carbon monoxide escaped combustion, but not more than 3 per cent. The gases contained in the chamber A had the composition :

O <sub>2</sub> .....	36 per cent.
CO <sub>2</sub> .....	62   "   "
CO .....	2   "   "

It is interesting to compare these results with those obtained by Professor Dixon in his experiments on carbon monoxide (Trans., 1896, 69, 784). Slightly impure mixtures of carbon monoxide and excess of oxygen were sparked, a flame travelled down the tube, and on

FIG. 3.



analysis it was found that quantities of carbon monoxide varying up to 50 per cent. remained unburnt. In another series of experiments, dried mixtures of carbon monoxide and oxygen were fired by means of carbon disulphide, and 13 per cent. of the carbon monoxide escaped combustion. Notwithstanding the fact that in these experiments ordinary molecular carbon monoxide was employed, the results are strikingly similar to those I have obtained with nascent carbon monoxide. This similarity is brought out in the following table, which shows the maximum amount of carbon monoxide left unburnt after explosion :

	Reaction accompanied by small heat evolution.	Reaction accompanied by greater heat evolution.	Reaction accompanied by still greater heat evolution.
Nascent CO	40 per cent. in limiting explosion of COS and oxygen.	9 per cent. in explosion of COS and oxygen with 4 per cent. CS <sub>2</sub> .	8 per cent. in explosion of Ni(CO) <sub>4</sub> and oxygen.
Molecular CO	50 per cent. in limiting explosion of CO and oxygen.	13 per cent. in explosion of CO and oxygen with 4 per cent. CS <sub>2</sub> .	

The comparison must not be pushed too far; it is quite impossible to have exactly the same conditions in any two experiments with partially purified substances, but the general results given in the table suggest that:

(1) The energy developed in the reaction has considerable influence in promoting the union of carbon monoxide and oxygen. This result may be simply due to the higher temperature to which the gaseous mixture is raised.

(2) The nascent condition of the carbon monoxide has no very great influence.

## II. *Interaction of Carbon Monoxide and Nascent Oxygen. Explosion of Chlorine Monoxide and Carbon Monoxide.*

This experiment was suggested during the discussion which followed the reading of the joint paper of Professor Dixon and myself in 1897. It was urged that "nascent" oxygen obtained in the decomposition of chlorine peroxide (used in the experiments in that paper) was not strictly atomic, and that a better oxide to use would be chlorine monoxide.

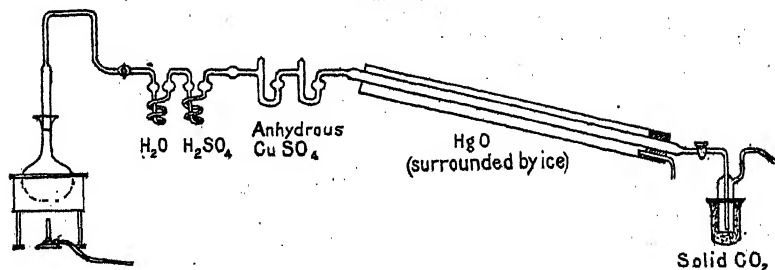
This has now been done, although the experimental difficulties proved to be considerable. I find that when dried mixtures of carbon monoxide and excess of chlorine monoxide are sparked, there is a violent explosion, but from 5—10 per cent. of the carbon monoxide remains unburnt. This is a much smaller quantity than was left in the case of the chlorine peroxide explosions (50—70 per cent.); it must, however, be borne in mind that a considerable amount of oxygen was present in the latter, and the results of the preceding section lead us to expect that the oxygen, by diminishing the intensity of the reaction, would increase the percentage of carbon monoxide unburnt. Another difference between the two cases lies in the fact that the explosion of chlorine monoxide is more violent than that of the peroxide, and a third is that in one case the 'nascent' oxygen is strictly atomic whilst in the other it is not.

The preparation of chlorine monoxide is not dangerous if the materials and apparatus are carefully freed from organic matter and no indiarubber connections are used. Chlorine, generated by acting on recrystallised potassium dichromate with pure hydrochloric acid, is passed through water, sulphuric acid, and two tubes containing anhydrous copper sulphate on pumice cleaned by treatment with aqua regia, and finally over precipitated mercuric oxide which has previously been dried for six hours at 400°. All parts of the apparatus were sealed together, and the delivery tube ground into the neck of the generating flask (Fig. 4).

The mercuric oxide is kept surrounded by ice; in my experiments it was prepared by adding caustic potash to a hot dilute solution of mercuric chloride which had been purified by dissolving in alcohol and reprecipitating by addition of water.\*

Prolonged drying is absolutely essential for the production of chlorine monoxide. If the experiment is properly carried out, chlorine is absorbed for about an hour, and then chlorine monoxide is evolved, a fairly large yield being obtained, although the operation is slow. No change in colour is observed in the solid contents of the tube, but as soon as air is admitted the solid darkens. On shaking it into dilute hydrochloric acid, there is a lively effervescence and some metallic mercury separates out; whatever the reaction between chlorine and mercuric oxide may be, it seems to involve something more than the simple formation, of either mercuric chloride or mercuric oxychloride.

FIG. 4.



If, however, the mercuric oxide has not been sufficiently dried, it is converted into a white mass and the gas obtained is chiefly oxygen with but little chlorine monoxide.

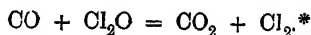
The chlorine monoxide was condensed in a bulb surrounded by solid carbon dioxide. When a sufficient quantity had collected, the carbon dioxide was removed and the liquid allowed to slowly evaporate. The first portion that comes off is chiefly chlorine, later fractions are, however, explosive and finally nearly pure chlorine monoxide is obtained. The liquid is reddish-brown in colour and the gas very closely resembles diluted nitrous fumes. Great care must be exercised in collecting samples of the gas; on one occasion, the sample tube used was not quite free from dust, having been wiped out with a soft duster which left a few specks of cotton on the walls, and immediately the gas came in contact with these there was a violent explosion which reached the liquid in the bulb, with the result that the bulb and the beakers surrounding it were completely pulverised. This is, however, the only accident I have had; if dust and organic matter

\* This affords a very rapid and easy method of purifying mercuric chloride.

are carefully excluded, liquid chlorine monoxide cannot be considered a dangerous body.

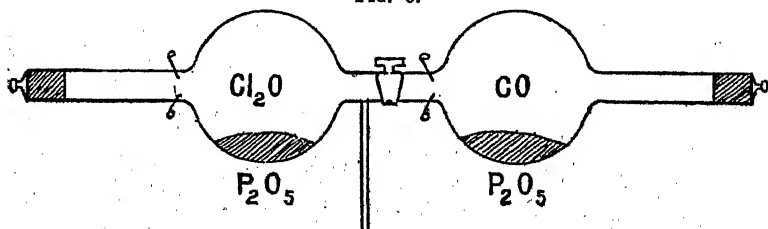
Mr. E. B. Le Mare has kindly given me much assistance in the preparation of this substance.

*Reaction with Carbon Monoxide.*—In the earlier experiments, mixtures of the two gases were made in the proper proportion, left to dry over distilled phosphorus pentoxide, and kept in the dark in an ice-chest. On sparking, no explosion took place. The contents of other tubes which had not been sparked were examined, and found to consist of carbon dioxide and chlorine, together with some unchanged carbon monoxide and chlorine monoxide; there was no oxygen, and I could detect no carbonyl chloride. At the end of 4—5 days, there was very little left of either carbon monoxide or chlorine monoxide. It follows then that at  $0^{\circ}$  and in the dark these two substances slowly react according to the equation:



The two gases were therefore dried separately for about 2 days at  $0^{\circ}$  and then allowed to diffuse into each other for one hour, the bulb con-

FIG. 5.



taining the heavier chlorine monoxide being placed so that the gas flowed down into the other. The tap separating the bulbs was then turned off and an electric spark passed in each. Explosions took place and the products were collected and analysed:

(1) Mixture before sparking: 1 vol. CO + 2 vols.  $\text{Cl}_2\text{O}$  (approximately).

Gases left after explosion and standing over mercury to absorb chlorine:

$\text{CO}_2 = 57$ ,  $\text{O}_2 = 39$ ,  $\text{CO} = 4$  per cent.

\* This is, I believe, the only instance known of direct oxidation of carbon monoxide at low temperatures. Remsen has shown that mixtures of carbon monoxide and ozone can be heated to temperatures at which ozone rapidly decomposes without forming carbon dioxide. This action can readily be explained if we suppose that carbon monoxide and chlorine monoxide unite, forming an additive compound which readily breaks up into chlorine and carbon dioxide. The unsaturated character of chlorine monoxide, as shown by its direct combination with sulphur, and of carbon monoxide, as shown by its readiness to unite with chlorine, would lead us to expect something of this kind.

(2) Mixture before sparking: 1 vol. CO + 2 vols. Cl<sub>2</sub>O (approximately).

Gases after explosion and absorption of chlorine:

CO<sub>2</sub> = 60, O<sub>2</sub> = 35, CO = 5 per cent.

In each case, about 6 or 7 per cent. of the carbon monoxide originally put in is left unburnt, although the drying was far from complete (30 hours only) and the explosion vigorous.

### III. *Interaction of Nascent Carbon Monoxide with Nascent Oxygen.*

This experiment was carried out in a manner precisely similar to that adopted by Dixon and Russell (*loc. cit.*). Chlorine peroxide and carbonyl sulphide were bubbled separately through sulphuric acid and allowed to mix, they were then passed into a eudiometer containing distilled phosphorus pentoxide. Pure chlorine peroxide, obtained by fractional distillation of the liquid, was used instead of the diluted gas. No cork or rubber connections were used in the apparatus, carefully ground-in glass connections being substituted.\*

The text-book method of preparing chlorine peroxide, namely, by the action of strong sulphuric acid on potassium chlorate, is dangerous and does not give a pure product. The method I adopted was essentially a modification by Schacherl (*Annalen*, 1881, 206, 68) of one described by Calvert and Davies (this Journ., 1859, 11, 193), which I have always found to be perfectly safe. 115 grams of recrystallised oxalic acid were dissolved in 200 c.c. of water, the solution cooled, 100 c.c. of strong sulphuric acid added, and the whole allowed to cool so slowly that large crystals were formed.† 25 grams of finely powdered recrystallised potassium chlorate were added, the mixture well shaken, and heated to 40–50° on the water-bath. The gases evolved—carbon dioxide, chlorine peroxide, and a trace of chlorine (Pebal and Schacherl, *Annalen*, 1882, 213, 113)—were dried by calcium chloride and passed into a receiver cooled by ice and salt where the chlorine peroxide condenses to a liquid having the colour of potassium dichromate. The liquid is comparatively stable, and I have repeatedly fractionated it without accident. It has, however, exploded under the following conditions:

- (1.) Contact with concentrated sulphuric acid.
- (2.) The mechanical shock occasioned by pouring fresh freezing mixture on to the containing bulb.

The explosions were violent; in one case the bulb was ground to a

\* The wires must be sealed into the wide part of the eudiometer; explosions brought about by the spark are not propagated in the narrow tubes at the ends.

† This is important, as when the cooling was rapid and the crystals small, the mixture frothed very much during the preparation.

fine powder, a duster wrapped round it torn to shreds, and a stout wooden box on which it was standing shattered.

It is, however, perfectly safe to blow gases, for example, carbon dioxide, through the liquid or to shake it about in a narrow tube (3 mm. diameter). The gas has been caused to explode:

(1.) By contact with organic matter, such as traces of impurity in sulphuric acid or phosphorus pentoxide.

(2.) By scratching the tube containing it with a file.

(3.) By shaking pieces of broken glass in it.

The explosions, however, always stop at narrow tubes.

The gas gradually decomposes over mercury, and is only slowly absorbed by caustic potash or soda; it will, in fact, bubble through solutions of these without much loss, and a moistened stick of caustic potash requires to be left for 10—12 hours in contact with the gas to effect complete absorption. Undistilled phosphorus pentoxide is acted upon, giving a red substance; it becomes hot and has even caused an explosion. Pure phosphorus pentoxide, however, is not affected; the gas can be kept over it for 2—3 days at  $0^{\circ}$  without much decomposition.

The mixtures of chlorine peroxide and carbonyl sulphide were allowed to dry for 24 hours in the ice chest and then exploded either by means of a spark or by heating in an air-bath; the gases lost their deep green colour and became colourless. When the explosion was brought about by sparking, carbonyl chloride could always be detected among the products, its pungent odour being readily recognisable even in presence of chlorine and sulphur dioxide; if the explosion were caused by gradual heating, I could never clearly detect any of the chloride. In other respects, the results were identical. The amounts of carbon monoxide obtained were:

1 vol. COS + $5\frac{1}{2}$ or 6 vols. $\text{ClO}_2$	No CO found
1 „ + 4 or $4\frac{1}{2}$ „	about $2\frac{1}{2}$ —4 per cent. of the COS is left as CO
1 „ + $1\frac{1}{2}$ (rather less) vols. $\text{ClO}_2$	„ 20 per cent. of the COS is left as CO

These results show that when carbon monoxide and oxygen are brought together, both being in the nascent condition and also heated by the flame of an explosion, combination is not complete. If longer drying of the chlorine peroxide were possible, no doubt a larger percentage of uncombined carbon monoxide would be found.

#### IV. *Inertness of pure Carbonyl Sulphide towards Oxygen.*

We have already seen that the further the purification of carbonyl sulphide is carried, the greater is the proportion left unburnt when

mixtures of carbonyl sulphide with excess of oxygen are sparked. This can only be interpreted as showing that pure carbonyl sulphide will not explode on sparking with oxygen. So far, only one such sample has been obtained, and I have not found any method of purification which can be relied upon to give a sufficiently pure gas. In mixtures of carbonyl sulphide and nitrous oxide (which explode if not purified), after standing for some weeks over pure sulphuric acid, and for a further lengthy period over phosphorus pentoxide, an electric spark produces no explosion. On now decanting the gaseous mixture into another eudiometer, adding a drop of water, and passing a spark, a violent explosion takes place.

### *Conclusions.*

The conclusions to be drawn from the above experiments are :

1. Pure carbonyl sulphide will not explode if sparked with oxygen.
2. If a small quantity of impurity is present, a flame traverses the whole tube on sparking the mixture, but combustion is not nearly complete; part of the carbonyl sulphide remains unburnt, and part is decomposed into carbon monoxide and sulphur, which likewise do not burn, although excess of oxygen and a small quantity of impurity are present. As, however, this quantity increases, combustion rapidly becomes more complete.

3. Mixtures of carbonyl sulphide and nitrous oxide require a larger quantity of impurity to cause combustion than mixtures of carbonyl sulphide and oxygen in the same circumstances. It seems probable that the quantity necessary for the latter mixture is also different from that required by mixtures of carbon monoxide and oxygen.

4. The state of affairs following on a violent reaction—such as explosion of carbon disulphide or chlorine monoxide, &c., has a very considerable influence in bringing about combination of carbon monoxide and oxygen. Whether this is a direct effect, or due to a heightening of the action of the "third substance," there is as yet little evidence. I can find no evidence that the nascent state, *per se*, is very effective. When the conditions were made as nearly as could be the same, there did not seem to be a great difference between the behaviour of nascent carbon monoxide and that of molecular carbon monoxide as studied by Dixon.

Finally, I wish to thank Professor Dixon for much kindly help and advice given during the progress of this research.

THE OWENS COLLEGE,  
MANCHESTER.

XXXV.—*Note on the Refraction and Magnetic Rotation of Hexamethylene, Chlorohexamethylene, and Dichlorohexamethylene.*

By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

A SPECIMEN of hexamethylene was obtained by one of us (Trans., 1898, 73, 932) by the long-continued fractional distillation of Galician petroleum and was believed at the time to be pure. Its molecular refraction and magnetic rotation were determined by Dr. W. H. Perkin, sen., and the data obtained by him were published in the paper.

It was afterwards found (Trans., 1899, 75, 873) that the hexamethylene could be partially, but not completely, frozen, and that it therefore contained a small quantity of another hydrocarbon, probably a heptane. By a series of fractional crystallisations, the hexamethylene was separated from the paraffin, and was finally found to melt practically constantly at  $+4.7^{\circ}$ . Dr. Perkin has redetermined the refraction and magnetic rotation of this pure specimen, and has very kindly sent us the results for publication:

*Hexamethylene.*

The magnetic rotation was as follows:

Temperature.	Specific rotation.	Molecular rotation.
$15.0^{\circ}$	0.9503	5.664

The calculated value for the molecular rotation is  $1.023 \times 6 = 6.138$ ; it will be seen, therefore, that the observed value differs from the calculated, being considerably lower.

The refractive power is given in the following table:

	Index of refraction.	Specific refraction.	Molecular refraction.
	$\mu$ .	$\frac{\mu-1}{d}$ .	$\frac{\mu-1}{d} p$ .
$H_a$ .....	1.42673	0.54552	45.824
$H_b$ .....	1.43416	0.55503	46.622
$H_\gamma$ .....	1.43861	0.56071	47.100

Dispersion,  $H_\gamma - H_a = 1.276$ .

The temperature was  $15^{\circ}$  and the density  $d$   $15^{\circ}/4^{\circ}$  was 0.78224.

Dr. Perkin has also redetermined the refraction and magnetic rotation of the specimens of monochlorohexamethylene and dichlorohexamethylene (Trans., 1898, 73, 932), because, although the rotation of the former was lower than he expected, and that of the latter was



about correct, the refractive values of both were higher than the calculated by nearly a unit. He points out that, generally, if the refractive value is high, the magnetic rotation is proportionately a good deal higher. The new results, however, confirm those previously obtained.

By an error, the calculated value for Cl displacing H in the molecular magnetic rotation was given in the paper referred to as 1.558 instead of 1.479 for the mono- and 1.391 for the di-displacement. The theoretical values for the two chlorine derivatives are therefore appended.

The values obtained by Dr. Perkin are as follows :

*Monochlorohexamethylene.*

Magnetic rotation :

Temp.	Spec. rot.	Mol. rot.	Previous result.	Diff.
13.5°	1.1171	7.501	7.478	0.023
6CH <sub>2</sub> = 6 × 1.023 .....				6.138
Cl disp. H as in monochloro-paraffins ...				1.479
				<hr/> 7.617
Mean observed value.....				7.489
				<hr/>
Difference .....				0.128

Refractive power :  $d_{15^\circ/4^\circ} = 0.97923$ .

	$\mu_{15^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}^p$	Previous numbers.	Diff.
H <sub>a</sub> .....	1.45472	0.46437	55.027	54.989	0.038
H <sub><math>\beta</math></sub> .....	1.46307	0.47289	56.038	56.008	0.030
H <sub><math>\gamma</math></sub> .....	1.46812	0.47805	56.649	56.604	0.045

*Dichlorohexamethylene.*

Magnetic rotation :

Temp.	Spec. rot	Mol. rot.	Previous result.	Diff.
13.5°	1.2307	8.955	8.905	0.05
6CH <sub>2</sub> = 6 × 1.023 .....				6.138
Cl <sub>2</sub> disp. H <sub>2</sub> as in CH <sub>2</sub> Cl <sub>2</sub> .....				2.782
				<hr/> 8.920
Mean observed value .....				8.930
				<hr/>
Difference ... ..				0.010

Refractive power:  $d_{15.2^\circ/4^\circ} = 1.16668$ .

	$\mu_{15.2^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}^2$	Previous numbers.	Diff.
H <sub>a</sub> .....	1.48556	0.41619	63.677	63.659	0.018
H <sub><math>\beta</math></sub> .....	1.49467	0.42400	64.872	64.853	0.019
H <sub><math>\gamma</math></sub> .....	1.50218	0.43044	65.857	65.800	0.057

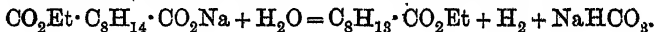
The values for the dispersion  $H_\gamma - H_a$  for monochlorohexamethylene, 1.622, and for dichlorohexamethylene, 2.180, differ but slightly from the corresponding values, 1.615 and 2.141, previously obtained.

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BRISTOL.

### XXXVI.—*Campholytic and Isolaunonic Acids.*

By JAMES WALKER and WILLIAM CORMACK.

IN former papers (Walker, *Trans.*, 1893, 63, 495; 1895, 67, 347), it was shown that when sodium ortho-ethyl camphorate was electrolysed in aqueous solution, an unsaturated ethereal product was obtained at the anode in accordance with the following empirical equation:



This ethereal product, when fractionated and hydrolysed, yielded two isomeric unsaturated acids of the formula  $\text{C}_8\text{H}_{13} \cdot \text{CO}_2\text{H}$ , one of which, campholytic acid, was a liquid, and the other, isolaunonic acid, a solid. These acids were also obtained by W. A. Noyes from  $\beta$ -camphoramic acid (*Amer. Chem. J.*, 1894, 16, 505; 1895, 17, 421), and isolaunonic acid in particular has recently been the subject of numerous investigations, chiefly by Blanc and by W. H. Perkin, jun.

By the action of alkalis on the dibromide of campholytic acid, a bromohydrocarbon is produced (*Trans.*, 1893, 63, 502), a decomposition which Fittig's researches have shown to be characteristic of  $\alpha\beta$ -dibromo-acids. Noyes found that the dibromide of isolaunonic acid undergoes a similar decomposition when neutralised with sodium carbonate, and was therefore led to regard the two unsaturated acids as stereoisomeric, a view which is strengthened by his discovery that campholytic acid is converted on standing with mineral acids into the isomeric isolaunonic acid. It is now generally admitted that isolaunonic acid is an unsaturated acid with the double bond in the  $\alpha\beta$  position with regard to the carboxyl group (Blanc, *Ann. Phys. Chim.*, 1894, 13, 181; Perkin, *Trans.*, 1898, 73, 810).

The relationship of campholytic and isolaunonic acids to camphoric acid is of the greatest importance in

determining the relative position of the carboxyl groups in the molecule of the latter substance, we adduce in the present paper some further data bearing on this point.

*Electrolysis of Sodium Ortho-methyl Camphorate.*

Since hydrobromic acid was used by Walker in the production of isolauronolic acid from the ester  $C_8H_{13}\cdot CO_2Et$ , it does not follow that ethyl isolauronolate is a direct product of the electrolysis of sodium ortho-ethyl camphorate, for the isolauronolic acid, according to Noyes's researches, might conceivably have been produced by the isomeric transformation of campholytic acid. In order to decide this point, we repeated the electrolysis of the alkali salt of a hydrogen ortho-alkyl camphorate.

The sodium ortho-ethyl salt used in former experiments was the crude product obtained by the direct addition of sodium ethoxide to camphoric anhydride in presence of ethyl alcohol. This substance was liable to contain a little of the allo-ethyl salt, for experience with the corresponding methyl compounds had indicated that a perfectly pure ortho-alkyl salt is not produced by the direct addition of camphoric anhydride to sodium alkyl oxide. To avoid any such source of uncertainty, we therefore in this case prepared pure hydrogen ortho-methyl camphorate, neutralised it with potassium carbonate, and electrolysed the potassium salt thus obtained.

Crude sodium ortho-methyl camphorate was obtained by the direct union of sodium methoxide and camphoric anhydride in presence of methyl alcohol according to the directions given by Walker (*Trans.*, 1892, 61, 1089). The corresponding hydrogen salt was liberated by hydrochloric acid, and dissolved out in ether. The residue from the ethereal solution crystallised on standing, and the crystals were freed from a slight syrupy admixture by spreading on a porous tile. The melting point of these crystals was  $73^\circ$ , that of the pure substance being  $77^\circ$ . Purification of large quantities of the substance by recrystallisation from most organic solvents is somewhat tedious (compare Wegscheider, *Monatsh.*, 1899, 20, 685), but we find that a single recrystallisation from 25 per cent. acetic acid yields practically pure hydrogen ortho-methyl camphorate. Thus 13 grams of the crude crystals, on warming with 100 c.c. of 25 per cent. acetic acid, gave a solution which deposited 12.5 grams of crystals having the melting point  $77^\circ$ .

The acid thus purified was dissolved along with the calculated quantity of potassium carbonate in about its own weight of water. Contrary to the behaviour of the sodium ethyl salt on electrolysis, the potassium methyl salt was found to yield an ethereal product only

with great difficulty. The chief reaction on the passage of an electric current is here the production of hydrogen at the cathode and oxygen at the anode with regeneration of the original salt. There is thus little loss of substance, but the quantity of electricity which must be passed in order to produce a given quantity of ethereal product is out of all proportion greater than the theoretical amount. We tried numerous variations of concentration, current strength, voltage, temperature, and size of electrodes, but always with the same result—the yield of ethereal product was constant, but extremely small for the magnitude of the current. It seemed to us possible that the difference might be due to the salt electrolysed in the present instance being quite pure, whilst the sodium ethyl salt previously employed had been impure. We therefore prepared a solution of crude sodium ortho-methyl camphorate by direct union of sodium methoxide with camphoric anhydride and submitted it to electrolysis, but no difference in the result was thereby obtained. It thus appears that the replacement of ethyl by methyl in this particular instance greatly increases the difficulty of obtaining an ethereal substance, the chief electrolytic action being the decomposition of water with production of oxygen and hydrogen. A current of 10 ampères for 45 hours produced only 85 grams of ethereal salts instead of the approximate theoretical amount of 2,800 grams. The yield of ethereal product, however, when referred to the amount of potassium ortho-methyl salt electrolysed, amounted to nearly 50 per cent. of the theoretical quantity.

The ethereal product of electrolysis was subjected to fractional distillation, and in accordance with previous experience in similar cases, separated roughly into a fraction of high and one of low boiling point, ebullition beginning at about  $190^{\circ}$ . As methyl isolauronolate boils at  $204^{\circ}$  under a pressure of 760 mm., the portion of lower boiling point was investigated for this substance. 10 grams of the oil mixed with 10 c.c. of methyl alcohol, 5 c.c. of water, and 10 grams of caustic potash, were heated on the water-bath for 1 hour. The bulk of the methyl alcohol was driven off by evaporation in an open vessel, and water was then added. The solution was next extracted with ether in order to remove any ethereal salt which had escaped hydrolysis, and acidified with hydrochloric acid. A dark green oil separated, which was at once taken up by ether, in order to remove it from contact with the mineral acid, the last traces of which were removed from the ethereal solution by washing with water. The crude acid obtained after evaporation of the ether was distilled with steam. A small quantity of an oil (campholytic acid) first passed over, and then a white solid crystallised in the condenser. The solid, after one crystallisation from light petroleum, was found to melt at  $135^{\circ}$ , and proved to be isolauronolic acid.

Since none of the above operations would suffice to convert campholytic into isolauronolic acid, it must be accepted that methyl isolauronolate is, along with methyl campholytate, a direct product of the electrolysis of potassium ortho-methyl camphorate.

*Optical Inactivity of Campholytic and Isolauronolic Acids.*

The optical character of isolauronolic acid being of importance in determining its constitution, we examined in the polarimeter a saturated solution of the acid prepared by electrolysis, using methyl alcohol as solvent. No rotation could be detected with certainty, and a similar result followed the examination of a saturated aqueous solution of the sodium salt. The isolauronolic acid prepared by electrolysis must therefore be accounted optically inactive.

The original campholytic acid derived from sodium ortho-ethyl camphorate by electrolytic decomposition was stated to have a specific rotation of  $[\alpha]_D -5^\circ$ . This rotatory power is comparatively slight for a derivative of camphor, and it therefore appeared of interest to ascertain if it were real, or merely due to the admixture of a strongly active impurity with an inactive substance. A certain degree of probability is lent to this view by the circumstance that the crude isolauronolic acid obtained by electrolysis is slightly active, and loses its rotation only on repeated crystallisation.

Since campholytic acid is a liquid, the only method employed for its purification was fractional distillation, a process which is in general useless for removing the last traces of impurity from a liquid of high boiling point, unless very large quantities of material are available. In order to attempt the purification by another method, we prepared a quantity of campholytic acid by electrolysis. An investigation of the salts of the acid showed that magnesium campholytate was susceptible of purification by recrystallisation from water. The crude campholytic acid from which the magnesium salt was prepared had the specific rotation  $[\alpha]_D -9.6^\circ$ . The magnesium salt obtained from this acid had also a well marked negative rotation. It was sparingly soluble in cold water, the saturated solution being of about 4 per cent. strength. The crude crystals were treated with successive small portions of hot water, allowed to cool, and filtered, the rotation of the filtrate being determined in each case. In three successive operations, the rotation of the filtrates in a 20 cm. tube were  $-5^\circ$ ,  $-2^\circ$ , and  $-1.2^\circ$  respectively, showing that the active substance was being removed by the water. The residual crystals were then reconverted into the acid, which now showed a specific rotation  $[\alpha]_D -2.7^\circ$ . Crystallisation had thus reduced the rotatory power to one-fourth of that of the crude acid, and to about one-half of the value for the campholytic acid originally

prepared. With a sufficiency of material to permit a thorough systematic recrystallisation of the magnesium salt, the activity would doubtless altogether disappear, that observed being apparently due to some very active impurity. This conclusion is justified by the fact that the campholytic acid which we succeeded in preparing from isolaunonic acid, is entirely destitute of optical activity.

A portion of the campholytic acid purified by recrystallisation of the magnesium salt was converted into isolaunonic acid by warming with 25 per cent. sulphuric acid. The isolaunonic acid was driven over by steam, dried, and recrystallised from light petroleum. A 12 per cent. solution of the acid thus obtained showed no rotation when examined in a 20 cm. tube by the aid of a polarimeter reading to  $0.01^\circ$ .

It thus appears that isolaunonic acid, whether prepared by Blanc's method from camphoric anhydride and aluminium chloride (Blanc, *loc. cit.*), by the electrolytic decomposition of ortho-alkyl camphorates, or by the isomeric transformation of campholytic acid, is optically inactive.

#### *Transformation of Isolaunonic Acid into Campholytic Acid.*

Whilst the conversion of campholytic acid into isolaunonic acid may be effected with great readiness by the action of mineral acids, the reverse transformation has not so far been brought about directly. We have found it possible, however, to pass in an indirect way from isolaunonic acid to campholytic acid.

Noyes (*Amer. Chem. J.*, 1895, 17, 427) ascertained that fuming hydrobromic acid acts on campholytic acid in presence of a little light petroleum to form a hydrobromide,  $C_8H_{14}Br \cdot CO_2H$ , from which campholytic acid could be recovered by the action of alkalis and subsequent acidification. This bromo-acid melted with decomposition at  $98-100^\circ$ , and on neutralisation yielded a small quantity of an indifferent compound, which we have proved to be a hydrocarbon. An  $\alpha\beta$ -acid like campholytic acid would naturally assume the bromine in the  $\beta$ -position on taking up hydrogen bromide, and Fittig has shown that  $\beta$ -bromo-acids yield hydrocarbons on neutralisation, so that the action affords a further proof that campholytic acid is an unsaturated acid with the double bond in the  $\alpha\beta$ -position.

Noyes also studied the action of hydrobromic acid on isolaunonic acid, and on one occasion obtained a hydrobromide containing the theoretical amount of bromine for the formula  $C_8H_{14}Br \cdot CO_2H$ , and melting at  $127-130^\circ$ . This hydrobromide he considered to be the true hydrobromide of isolaunonic acid. He was, however, unable to prepare the substance a second time, and although operating under a

great variety of conditions, always obtained a bromo-acid of lower melting point.

We have repeated these experiments, since it appeared to us possible that some light might be thrown on the relation of the two isomeric unsaturated acids by the behaviour of the corresponding hydrobromides. Campholytic acid (2 grams), on being shaken up with 5 c.c. of hydrobromic acid solution saturated at  $0^{\circ}$ , became crystalline after one hour, and the solid after recrystallisation from light petroleum was found to be identical with the hydrobromide of campholytic acid prepared by Noyes. The melting point varied, according to the mode of heating, from  $88^{\circ}$  to  $102^{\circ}$ , and was always accompanied by darkening and evolution of gas.

On treating isolauronolic acid under similar conditions, we found that the hydrogen bromide was much more slowly absorbed. After the acids had remained in contact for 7 days, the solid was found to contain the theoretical quantity of bromine, but the product, instead of being Noyes's acid melting at  $127-130^{\circ}$ , proved to be identical with the hydrobromide of campholytic acid. This result was repeatedly obtained, and finally we prepared a considerable quantity of the hydrobromide of campholytic acid by keeping isolauronolic acid in contact with hydrobromic acid solution, which was retained at the saturation point by the passage of a slow current of the gaseous acid. The addition of hydrogen bromide could be effected in this way in about 24 hours, the bromo-acid then containing the calculated quantity of bromine, and melting with decomposition at a little over  $90^{\circ}$ .

The quantity of bromine in the bromo-acid was at first estimated in sealed tubes by Carius's method. We found, however, that the determination could be effected much more simply by decomposing a weighed quantity of the acid with caustic soda, all the bromine in the acid being thereby converted into sodium bromide, the bromine in which was afterwards estimated by titration according to Volhard's method. Too high results are obtained if the acid is recrystallised from light petroleum alone, since free hydrogen bromide clings to the crystals with remarkable persistence. This source of error may, however, be easily avoided by washing the crystals with a small quantity of cold water prior to drying and recrystallisation.

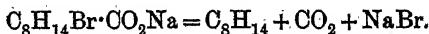
In order to prove that the bromo-acid obtained from isolauronolic acid is the hydrobromide of campholytic acid, we treated a quantity of it with excess of caustic soda solution. A small quantity of an indifferent oil separated as the acid dissolved, and this we removed by distillation with steam, the substance being extremely volatile. The steam distillate was extracted with ether, the ethereal solution dried, and the ether distilled off. The residual oil distilled completely

between  $108^{\circ}$  and  $110^{\circ}$  at the ordinary pressure, and gave the following figures on analysis:

0.0484 gave 0.1540  $\text{CO}_2$  and 0.0542  $\text{H}_2\text{O}$ .  $\text{C} = 86.7$ ;  $\text{H} = 12.4$ .

$\text{C}_8\text{H}_{14}$  requires  $\text{C} = 87.3$ ;  $\text{H} = 12.7$  per cent.

From its composition and boiling point, the substance is thus *isolaurelene*, formed according to the equation:



The hydrocarbon showed no optical activity when examined in a delicate polarimeter.

The formation of this hydrocarbon leaves no doubt that the bromine is in the  $\beta$ -position, as one would indeed expect from the mode of formation of the bromo-acid.

The solution of the sodium salt, from which the hydrocarbon had been removed by distillation with steam, was carefully acidified with hydrochloric acid and the oil which separated at once, dissolved by shaking up with ether. After washing with water, drying, and distillation of the ether, an oily acid remained, which, on combustion, yielded the following numbers:

0.1242 gave 0.3204  $\text{CO}_2$  and 0.1030  $\text{H}_2\text{O}$ .  $\text{C} = 70.35$ ;  $\text{H} = 9.21$ .

$\text{C}_9\text{H}_{14}\text{O}_2$  requires  $\text{C} = 70.13$ ;  $\text{H} = 9.09$  per cent.

The acid had thus the composition of campholytic acid, and its identity was proved by the conversion of a portion of it into isolauronolic acid by warming with 25 per cent. sulphuric acid.

A 60 per cent. ethereal solution of the campholytic acid, prepared from isolauronolic acid by the above method, gave a rotation in a 10 cm. tube which was less than a hundredth of a degree. The acid is therefore optically inactive.

#### *Hydrobromide of Isolauronolic Acid.*

Our first attempts to prepare the hydrobromide of isolauronolic acid were attended with but little success. If fuming hydrobromic acid is employed, the action proceeds in such a way that it is impossible to find a point at which the theoretical amount of hydrogen bromide has been taken up, and at which the isomeric transformation into the hydrobromide of campholytic acid is not yet effected. With weaker hydrobromic acid, however, the absorption is comparatively slow, and it was found to be possible, by stopping the action somewhat before the theoretical amount of hydrogen bromide had been absorbed, to isolate the hydrobromide of isolauronolic acid. The manner of operating which gave the most uniform results was as follows. The



islauronolic acid was allowed to remain in contact in a test-tube with 50 per cent. hydrobromic acid in quantity little more than sufficient to cover it. The absorption, which is at first moderately rapid, is speedily retarded by the diminution of the strength of the hydrobromic acid solution as absorption progresses, and apparently a weak acid is unable to effect the isomeric transformation. At the expiration of 24 hours, the solution was again brought to the saturation point by passing in hydrogen bromide, and the action allowed to proceed. This operation was repeated at intervals of 24 hours until the solid contained between 25 and 30 per cent. of bromine, the theoretical amount being 34 per cent. The crystalline mass then consisted chiefly of the hydrobromide of islauronolic acid along with a comparatively small amount of untransformed islauronolic acid. Now islauronolic acid is much less soluble in light petroleum than its hydrobromide. If therefore the dried and washed crystalline mass is dissolved in the minimum quantity of this solvent, the first portion which separates out on crystallisation contains the bulk of the islauronolic acid, and the residual liquid yields the practically pure hydrobromide. Thus a mixture which initially contained 28 per cent. of bromine, and melted at  $127-130^{\circ}$ , yielded a first crop of crystals containing 11 per cent., and a second crop containing 32 per cent. of bromine. Heating is to be avoided in the recrystallisation, as the hydrobromide tends to lose hydrogen bromide when warmed in light petroleum. The melting point of the substance prepared and purified in this way is  $132-133^{\circ}$ , the fusion being unattended by any appreciable darkening or decomposition.

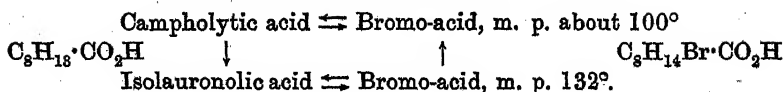
In order to ascertain if this bromo-acid were in reality the hydrobromide of islauronolic acid, we subjected it to treatment with caustic soda. As in the case of the isomeric compound, a small quantity of an indifferent substance was produced, but the acid precipitated from the alkaline solution by hydrochloric acid was solid, and not liquid as in the former instance. On recrystallisation from light petroleum, the acid melted at  $135^{\circ}$ , and had the other properties of islauronolic acid. A combustion resulted as follows:

0.0976 gave 0.2512  $\text{CO}_2$  and 0.0842  $\text{H}_2\text{O}$ .  $\text{C} = 70.2$ ;  $\text{H} = 9.5$ .

$\text{C}_9\text{H}_{14}\text{O}_2$  requires  $\text{C} = 70.1$ ;  $\text{H} = 9.1$  per cent.

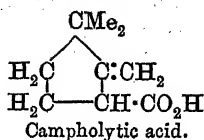
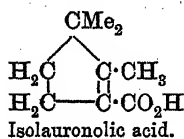
There is thus no doubt that the bromo-acid melting at  $132^{\circ}$  is the hydrobromide of islauronolic acid, as that melting at about  $100^{\circ}$  is the hydrobromide of campholytic acid.

It is now possible to convert any one of the four following acids directly or indirectly into any other in the manner indicated by the arrows in the diagram.



*Isomerism of Campholytic and Isolauronolic Acids.*

Blanc has recently suggested (compare Noyes, *Ber.*, 1900, 33, 57) that campholytic and isolauronolic acids are structural isomerides, and has assigned to them the following formulæ based on the Perkin-Bouveault formula for camphoric acid :

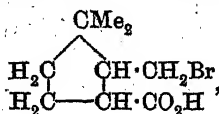


The formula for isolauronolic acid is satisfactory, inasmuch as it readily accounts for its electrolytic formation, its general chemical properties as an  $\alpha\beta$ -unsaturated acid, and its optical inactivity. The formula for campholytic acid, on the other hand, whilst it accounts simply for the electrolytic production of the acid, must be rejected for the following reasons :

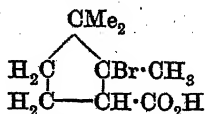
(1) Campholytic acid is not a  $\beta\gamma$ -acid as the formula indicates, but an  $\alpha\beta$ -acid, as is proved by the production of isolaurulene,  $\text{C}_8\text{H}_{14}$ , from its hydrobromide, and bromoisolaurulene,  $\text{C}_8\text{H}_{13}\text{Br}$ , from its dibromide. A  $\beta\gamma$ -acid under the same conditions would yield a lactone and a bromolactone respectively.

(2) An acid possessing Blanc's formula has an asymmetric carbon atom, and would in all probability be endowed with powerful optical activity, whereas campholytic acid is apparently inactive.

(3) The hydrobromide of an acid having Blanc's formula would be :

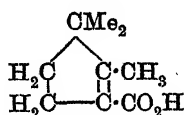


and it is inconceivable that such an acid could be formed from the hydrobromide of isolauronolic acid



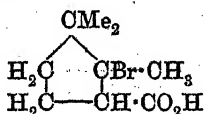
by isomeric transformation under the influence of hydrobromic acid in the cold (this vol., p. 379).

All these difficulties disappear if we consider campholytic and isolaunonic acids to be stereoisomerides having the structural formula :



Campholytic and isolaunonic acids.

Here the acids are both represented as  $\alpha\beta$ -acids and optically inactive, in accordance with their actual behaviour. The difference between them would merely be caused by the methyl and carboxyl groups being in the one case on the same side of the double bond, and in the other case on different sides. The difference between the stereoisomeric bromides :



would similarly be caused by these two groups being on the same or different sides of the plane of the ring. Thus the isomeric transformation of the acids themselves and of their hydrobromides can be easily explained.

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DUNDEE.

### XXXVII.—*Configuration of the Camphoric Acids.*

By JAMES WALKER and JOHN K. WOOD.

It is generally agreed that the molecule of camphoric acid contains two, and only two, asymmetric carbon atoms, that these carbon atoms are links in a closed carbon chain, and that each of them has a carboxyl group attached to it (compare Aschan, *Struktur- und Stereochemische Studien in der Camphergruppe*, Helsingfors, 1895). It is further known that the asymmetric carbon atoms are not similar to each other, so that there can be no optical inactivity by internal compensation. In order to distinguish between these two asymmetric atoms, we may employ the prefixes *ortho*- and *allo*-, which are commonly used in application to the two carboxyl groups. Thus we shall speak of the asymmetric carbon atom to which the *ortho*-carboxyl group is attached as the *ortho*-carbon atom, and of that to which the *allo*-carboxyl group is united as the *allo*-carbon atom.

We may then express the possible stereoisomeric camphoric acids as follows, the letters R, L denoting the opposite configurations of the ortho-atom, and the letters R', L' the opposite configurations of the allo-atom:

	I.	II.	III.	IV.
Ortho .....	R	L	R	L
Allo .....	R'	L'	L'	R'
	V. Inactive mixture.		VI. Inactive mixture.	

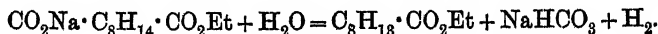
According to this scheme, there should therefore exist four optically active camphoric acids and two inactive mixtures formed from the two pairs of optical antipodes. All of these isomerides are known, and the following table indicates their names and characteristic properties, the data being chiefly taken from Aschan (*loc. cit.*).

<i>d</i> -Camphoric acid, m. p. 187°. [ $\alpha$ ] <sub>D</sub> + 47·8°	<i>l</i> -Camphoric acid, m. p. 187°. [ $\alpha$ ] <sub>D</sub> - 47·8°
<i>i</i> -Camphoric acid, m. p. 204°.	
<i>d</i> -Isocamphoric acid, m. p. 171—172°. [ $\alpha$ ] <sub>D</sub> + 47·1°	<i>l</i> -Isocamphoric acid, m. p. 171—172°. [ $\alpha$ ] <sub>D</sub> - 47·1°
<i>i</i> -Isocamphoric acid, m. p. 191°.	

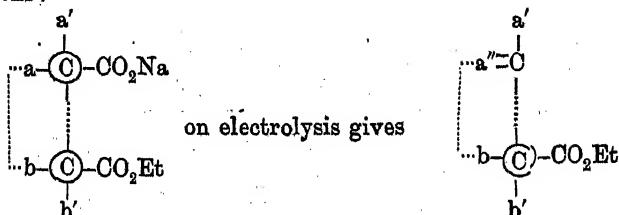
The rotations given are true for 10 per cent. solutions of the acids in absolute alcohol, and although they may vary somewhat with the concentration and the nature of the solvent, the numbers given in all probability indicate the correct relative position of the various acids with regard to their optical activity. Since *d*-camphoric acid has the largest positive rotation, we must assume that it has the configuration RR', and consequently that *l*-camphoric acid has the configuration LL'. The configurations RL' and LR', therefore remain for the formulæ of the two active isocamphoric acids, but further information must be acquired before we can assign either of these to any particular acid. A conceivable mode of gaining the requisite information is as follows. Let one of the asymmetric carbon atoms, say the ortho-carbon atom, lose its asymmetry, the other remaining asymmetric. If, when this operation is carried out, the product from *d*-camphoric acid is identical with that from *l*-isocamphoric acid, the configuration of the allo-carbon atom in these acids is the same; if, on the other hand, the product from *d*-camphoric acid is the optical antipode of that from *l*-isocamphoric acid, the allo-carbon atoms in these acids have opposite configurations.

The electrolysis of the sodium alkyl salts of the camphoric acids

affords a simple method of splitting off either of the carboxyl groups in the molecule at will, the action occurring according to the equation



The  $\text{CO}_2\text{Na}$  group and the hydrogen atom lost by the camphoric molecule come from neighbouring carbon atoms, in accordance with the general rule established by Kolbe and by Crum Brown and Walker, so that the ethyl ester of the unsaturated acid produced by the electrolysis contains only one asymmetric carbon atom. The change taking place on electrolysis may best be represented by the following scheme, which embodies the well grounded conclusions referred to at the beginning of this paper, and makes no further assumptions:



When sodium ortho-ethyl camphorate is electrolysed, the unsaturated products of the electrolysis are inactive, so that no conclusion as to the configuration can be drawn from them (see preceding paper). When sodium allo-ethyl camphorate, on the other hand, is submitted to electrolysis, the unsaturated esters thereby produced have a strong positive rotation. If, therefore, we find that the unsaturated esters derived from the electrolysis of sodium allo-ethyl *l*-isocamphorate have a strong positive rotation, we may conclude that the allo-carbon atom in it has the same configuration as the allo-carbon atom in *d*-camphoric acid. On performing the experiment, we found that this was actually the case, so that until well established evidence to the contrary is forthcoming, we may give the following configurations to the four active camphoric acids:

	<i>d</i> -Camphoric.	<i>l</i> -Camphoric.	<i>d</i> -Isocamphoric.	<i>l</i> -Isocamphoric.
Ortho.....	R	L	R	L
Allo .....	R'	L'	L'	R'

If at any future time it should be found that the camphoric acids have a slightly lower rotatory power than the isocamphoric acids, instead of slightly higher, as at present appears to be the case, the configurations of the camphoric and isocamphoric acids of similar rotations will have to be interchanged. But however this may be, the configurations, as far as stereochemical formulæ are concerned, are

definitely fixed, as will be shown in the following paper (this vol., p. 395).

*l*-Isocamphoric Acid.

We first prepared this acid from ordinary camphoric acid by Aschan's method (*loc. cit.*, 145), which consists in heating the acid with a mixture of equal parts of glacial acetic acid and concentrated hydrochloric acid to effect the isomeric transformation, and then separating the isomeric acids by means of acetyl chloride. As this method involves the use of sealed tubes, and gave in our hands a yield of only 15 per cent. of the isocamphoric acid, we abandoned it after a time in favour of Marsh's method, which we found on the whole to be more convenient. Marsh (*Chem. News*, 1889, 60, 307) prepared the acid from the camphoryl chloride obtained from *d*-camphoric acid by the action of phosphorus pentachloride. According to Marsh, this chloride, on treatment with warm water, gives a precipitate which consists of about equal parts of *d*-camphoric anhydride and of *l*-isocamphoric acid. We experienced some difficulty in ascertaining the proper conditions for obtaining a good yield of *l*-isocamphoric acid in this way, and finally adopted the following method as giving the best results. Camphoryl chloride was added very gradually to twenty times its weight of water at a temperature of about 80°, the liquid being constantly agitated by means of a Witt stirrer during the whole period of mixing. When all the chloride had been added, the liquid was immediately filtered, and on cooling the filtrate a crystalline deposit separated, which consisted of crude *l*-isocamphoric acid. A further small portion of the crude acid was obtained by treating the residue on the filter with weak sodium carbonate solution and acidifying the extract. We generally worked with portions of 10 grams of camphoryl chloride, and from 100 grams of *d*-camphoric acid obtained about 25 grams of *l*-isocamphoric acid. This acid, however, was still impure, and was therefore treated with acetyl chloride in order to convert the *d*-camphoric acid with which it was mixed into the corresponding anhydride, the *l*-isocamphoric acid being thereby unaffected. When the acetyl chloride had evaporated, the residue was extracted with sodium carbonate solution in the cold, the solution acidified, and the precipitated acid recrystallised from hot water. The acid then melted at 172.5°, and had the specific rotation  $[\alpha]_D -46.2^\circ$  in 10 per cent. solution in absolute alcohol.

As all the acids closely related to camphor have a low dissociation constant, this magnitude was determined for *l*-isocamphoric acid in order to ascertain if it presented a similar anomaly. In the following table, which gives the results of the conductivity measurements at 25°,

$v$  represents the dilution in litres,  $\mu$  the molecular conductivity,  $m$  the degree of dissociation, and  $k$  the dissociation constant.

*l-Isocamphoric acid.*

$\mu_{\infty} = 352.$

$v.$	$\mu.$	100 $m.$	100 $k.$
70.5	11.74	3.33	0.00160
141	16.30	4.63	159
282	23.01	6.54	162
564	31.78	9.03	159

Mean..... 0.00160

The constant for *d*-camphoric acid is 0.00225. As might be expected, the dissociation constant of the acid which forms an anhydride is greater than that of the isomeric acid which forms no anhydride, for, other things being equal, the power to form an anhydride indicates proximity of the carboxyl groups, which brings in its train reinforcement of their acid character and consequent increase in the dissociation constant. Whilst, therefore, the constant of *l*-isocamphoric acid falls into its proper place with respect to that of other acids derived from camphor, it is decidedly small for the constant of a dibasic acid (compare this vol., p. 396).

*Ethyl Esters of l-Isocamphoric Acid.*

Friedel (*Compt. rend.*, 1891, 113, 891) prepared the ethyl esters of *l*-isocamphoric acid and briefly described their properties. As it was necessary that we should obtain these substances in order to prepare the sodium allo-ethyl salt for electrolysis, we purified them at the various stages and as far as possible adopted methods of preparation different from those employed by Friedel, in order that a comparison with his results might be effected.

*Hydrogen Ortho-ethyl l-Isocamphorate.*—Friedel prepared this substance by direct esterification of the acid with ethyl alcohol and hydrochloric acid. We repeated his experiment and can confirm his results. We found it more convenient, however, to use sulphuric acid instead of hydrochloric acid as the catalysing agent. The acid (10 grams), alcohol (50 c.c.), and sulphuric acid (2.5 c.c.) were heated together on a water-bath for 6 hours; the bulk of the alcohol was then distilled off and water added to the residue. The product separated out as an oil which quickly solidified, and was removed from the aqueous liquid by solution in ether. After drying with calcium chloride and evaporation of the ether, the hydrogen ethyl salt crystallised on cooling, and was purified by recrystallisation from light petroleum. The acid treated in this way yielded almost its own weight of purified

hydrogen ethyl salt, which melted at  $73.5^{\circ}$ , the melting point given by Friedel being  $75^{\circ}$ .

0.1145 gram required 20.35 c.c. of  $N/40$  baryta solution for neutralisation. Calculated 20.1 c.c.

The specific rotation of a 10 per cent. solution of the substance in absolute alcohol was  $[\alpha]_D -46.28^{\circ}$ . Friedel, for the substance in the superfused state, found  $[\alpha]_D -49.62^{\circ}$ .

A determination of the dissociation constant resulted as follows:

*Hydrogen ortho-ethyl l-isocamphorate.*

$\mu_{\infty} = 350.$			
<i>v.</i>	$\mu.$	100 <i>m.</i>	100 <i>k.</i>
244	13.82	3.95	0.00066
488	19.05	5.44	64
Mean.....			0.00065

Walker (Trans., 1892, 61, 715) found that the hydrogen ethyl salts of dibasic organic acids had dissociation constants less than those of the acids themselves in the ratio of 1 to 2.3 on the average. The ratio of the constant of the hydrogen ortho-ethyl salt to that of *l*-isocamphoric acid is here 1 to 2.5, so that there is no divergence from the general rule.

*Diethyl l-Isocamphorate.*—Friedel prepared this ester by interaction of the silver salt and ethyl iodide. The same substance may be readily obtained by the action of ethyl bromide on the potassium ethyl salt or on the dipotassium salt. The dipotassium salt was heated with six times its weight of absolute alcohol and a slight excess of ethyl bromide in a securely corked soda-water bottle at  $100^{\circ}$  during 5 hours. The potassium bromide which had separated was removed by filtration, and the alcohol, together with the excess of ethyl bromide, by distillation. The residual oil was dissolved in ether and the ethereal solution well washed first with dilute alkali and then with water. After the ethereal solution had been dried with calcium chloride, the ether was distilled off and the residue distilled under diminished pressure. The yield was almost theoretical.

0.1221 gave 0.2949  $\text{CO}_2$  and 0.1046  $\text{H}_2\text{O}$ .  $\text{C} = 65.8$ ;  $\text{H} = 9.5$ .

$\text{C}_{14}\text{H}_{24}\text{O}_4$  requires  $\text{C} = 65.6$ ;  $\text{H} = 9.4$  per cent.

The specific rotation at  $16^{\circ}$  was found to be  $[\alpha]_D -50.4^{\circ}$  for a 10 per cent. solution in absolute alcohol. The specific rotation of the liquid diethyl ester itself was somewhat less than this, namely,  $[\alpha]_D -49.8^{\circ}$ . Friedel for the liquid substance gives  $[\alpha]_D -48.5^{\circ}$ .

*Hydrogen Allo-ethyl l-Isocamphorate.*—The diethyl ester was mixed in



alcoholic solution with a quantity of caustic potash exactly sufficient for its half hydrolysis. The mixture was allowed to remain at the ordinary temperature for 24 hours, after which it was heated on the water-bath for 45 minutes. The alcohol was then distilled off and water added. In order to remove any unchanged diethyl ester, the aqueous solution was extracted with ether. On acidification, a yellow oil separated, which was taken up in ether, dried, and after evaporation of the ether distilled under 12 mm. pressure, practically all coming over at 176°. The distillate was a pale yellow, very viscous liquid of specific gravity 1.092 at 16°.

0.0872 required 15.5 c.c. of *N*/40 baryta for neutralisation. Calculated 15.3 c.c.

That the hydrogen allo-ethyl salt contained little or no hydrogen ortho-ethyl salt as an admixture was shown by its behaviour towards alcoholic potash. The ortho-ethyl salt is easily hydrolysed by this reagent, but we found that the allo-ethyl salt, after treatment with excess of alcoholic potash for 24 hours at the boiling point of the solution, was practically unchanged, the original oil being regained on acidification.

The distilled substance in 10 per cent. alcohol solution had a specific rotation of  $[\alpha]_D - 22.9^\circ$ .

#### *Electrolysis of Potassium Allo-ethyl l-Isocamphorate.*

A concentrated solution of potassium allo-ethyl *l*-isocamphorate was electrolysed with a current of about 4 ampères, the temperature being kept below 35°. An oil speedily separated which on completion of the electrolysis was removed from the aqueous solution by means of ether. The residue left after evaporation of the ether was a yellow oil which had a specific gravity of 1.015 and a specific rotation of  $[\alpha]_D + 5.93^\circ$ . The electrolysis of a strongly laevorotatory salt of a laevorotatory acid had thus yielded a dextrorotatory ester.

The portion of the ester of lowest boiling point from ordinary camphoric acid was that in which the ethyl ester of allo-campholytic acid was found. The intermediate fractions yielded a ketodihydro-allo-campholytic acid, which has since been termed camphononic acid, and the highest fractions yielded the diethyl ester of allo-camphothetic acid. The two former substances have only the allo-asymmetric carbon atom in the molecule, the asymmetry of the ortho-carbon atom having been destroyed.

We should expect therefore to gain most information from the rotation of the portions of lowest boiling point of the product derived from *l*-isocamphoric acid. The quantity of electrolysed product at our

disposal was too small to admit of a satisfactory fractional distillation, but an attempt was made to effect at least a partial separation of the various substances whose formation might be expected.

The first fraction we obtained boiled at about  $200^{\circ}$ , and had a specific rotation of  $[\alpha]_D + 20.9^{\circ}$ . The highest fraction had a rotation of  $[\alpha]_D - 1^{\circ}$ , and an intermediate fraction a rotation of  $[\alpha]_D + 8.5^{\circ}$ . The impurities in the fraction of lowest boiling point have therefore a small positive or even a negative rotation, so that the value of the positive rotation actually obtained for the first fraction is undoubtedly too low.

When the potassium ethyl salt of ordinary camphoric acid was electrolysed under as nearly as possible the same conditions as we here employed, the fraction of lowest boiling point had a specific rotation of  $[\alpha]_D + 29.8^{\circ}$ . There is thus a distinct approximation of the corresponding fractions from ordinary *d*-camphoric acid and *l*-isocamphoric acid, and we think ourselves justified in concluding that the allo-asymmetric carbon atom has the same configuration in both compounds, since if it had the opposite configuration, the rotation of the product would have a value of  $-30^{\circ}$ , instead of a positive rotation of nearly that magnitude.

The fraction of lowest boiling point here obtained is of course not pure ethyl allo-campholytate, but a mixture of this with ethyl camphonate from which separation by distillation was rendered impossible by the small quantity at our disposal. Combustion analyses yielded numbers intermediate between those required by the two esters, and the other properties of the liquid were such as would be shown by a mixture of the two substances.

UNIVERSITY COLLEGE,  
DUNDEE.

### XXXVIII.—*The Constitution of Camphoric Acid.*

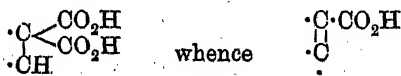
By JAMES WALKER.

In 1893 (Trans., 63, 495), I showed that the campholytic acid derived from sodium ortho-ethyl camphorate by electrolysis was an  $\alpha\beta$ -unsaturated acid, this conclusion being based on the fact that its dibromide decomposed on neutralisation according to the following equation :

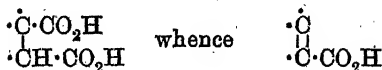


a behaviour which Fittig had proved to be characteristic of the dibromides of such acids. Now, as appears from the researches of

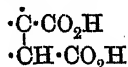
Kolbe and of Crum Brown and myself, when an unsaturated compound is formed on the electrolysis of a salt of a carboxylic acid, the acid loses the groups  $\text{CO}_2\text{H}$  and  $\text{H}$  from neighbouring carbon atoms, the double bond in the unsaturated compound being thus between the  $\alpha$ - and  $\beta$ -carbon atoms, as reckoned from the carboxyl group which has disappeared. The double bond of campholytic acid then is in the  $\alpha\beta$ -position with regard to the carboxyl group of the camphoric acid which has disappeared on electrolysis; but it is also in the  $\alpha\beta$ -position with regard to the carboxyl group, which remains after electrolysis. This gives us only two possibilities for the relative position of the carboxyl groups in the camphoric acid molecule. Either the molecule contains the group



or the group



These groupings, and no others, fulfil the required conditions, but the first is inadmissible, since it represents camphoric acid as a malonic acid derivative, which is altogether at variance with the known facts. There remains therefore only the conclusion (*loc. cit.*, 509) that the camphoric acid molecule contains the complex

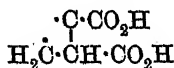


This conclusion, although it received immediate confirmation from the work of Noyes in 1894, was not generally accepted at the time, chiefly, no doubt, on account of the apparent difficulty in explaining the formation of camphanic acid from camphoric acid (compare *Trans.*, 1895, 67, 345).

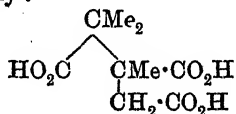
If exception is taken to the reasoning given above, it can only be on the ground that campholytic acid is not an  $\alpha\beta$ -unsaturated acid, that it is not a direct product of the electrolysis, or that the carboxyl group and hydrogen atom which are removed on electrolysis do not leave the molecule from neighbouring carbon atoms. The second and third of these points will be discussed later in connection with Perkin's formula for isolaunonic acid. With regard to the first, reference need only be made to the decomposition of the hydrobromide of campholytic acid on neutralisation (this vol., p. 380), and to the nature of the isomerism with isolaunonic acid (p. 382), which is universally admitted to be an  $\alpha\beta$ -unsaturated acid. The reasoning is further

strengthened by the proof that isolaunonic acid itself is, along with campholytic acid, a direct product of the electrolysis (this vol., p. 376).

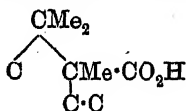
An investigation as to the products of electrolysis of potassium alloethyl camphorate (Trans., 1895, 67, 337; 1896, 69, 248), permitted a further conclusion to be drawn, namely, that camphoric acid contained the complex



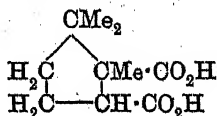
Now Perkin and Thorpe (Trans., 1897, 71, 1169), by their synthesis of camphoronic acid, a product of the oxidation of camphoric acid, proved conclusively that this acid has the constitution which had been suggested by Bredt, namely:



Camphoric acid therefore must contain the complex

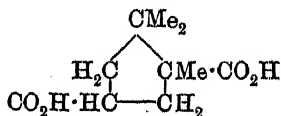


which, when combined with the complex derived from the behaviour of the electrolytic products, yields the Perkin-Bouveault formula,



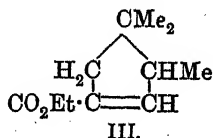
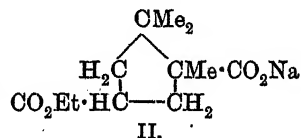
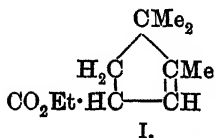
for the acid itself.

This formula was first suggested by Perkin, and afterwards, apparently independently, by Bouveault. Perkin, however, was led by his own experiments (Trans., 1898, 73, 796) to favour another formula which was proposed by him at the same time, namely,



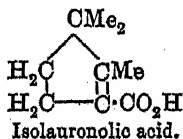
The behaviour of dihydro-isolaunonic acid chiefly weighed with Perkin in preferring this to the Perkin-Bouveault formula, but, as Blanc has shown (*Bull. Soc. Chim.*, 1899, [iii], 21, 830), Perkin's observations are open to a totally different interpretation from that put upon them by the author, and on the whole tell in favour of the Perkin-Bouveault formula.

That Perkin's second formula is irreconcilable with the results of electrolysis is plain from the fact that it does not contain a complex with the carboxyl groups in the ortho-position relatively to each other. If the electrolysis of the sodium ethyl salt of an acid having Perkin's formula (II) occurred in the ordinary way, the ethyl ester of the unsaturated acid thereby produced should have formula I. Now this acid is a  $\beta\gamma$ -unsaturated acid, and Perkin himself attributes the formula marked III to isolauronolic acid,



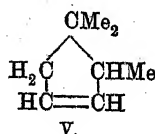
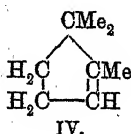
which, along with its stereoisomeride, campholytic acid, is the substance actually produced. That an ester having formula III should be formed directly from a substance having formula II is in the highest degree improbable, and that it should be formed by the isomeric transformation of the acid having formula I is almost equally unlikely, for not only is the electrolysis conducted at the ordinary temperature and in a solution which is, at most, feebly alkaline with sodium hydrogen carbonate, but the ester produced immediately separates from the aqueous liquid, and is thus exposed to the action of no chemical agents whatever. The improbability of an isomeric transformation of a primary  $\beta\gamma$ -product into an  $\alpha\beta$ -acid is still further increased by the fact that the  $\beta\gamma$ -acids obtained from the electrolysis of potassium allo-ethyl camphorate show no tendency whatever, under the experimental conditions, to pass into  $\alpha\beta$ -acids.

The formula for isolauronolic acid (and campholytic acid) derived from the Bouveault-Perkin formula for camphoric acid is



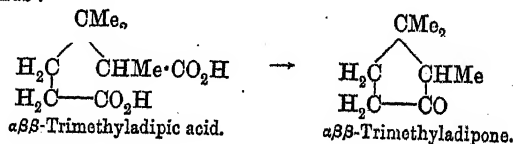
As Blanc has pointed out, this formula has no asymmetric carbon atom, and the acid corresponding to it must therefore be inactive. The isolauronolic acid formula of Perkin, on the other hand, has one asymmetric carbon atom, so that the corresponding acid should exhibit optical activity, unless it be a racemic mixture. Now, the isolauronolic acid prepared from camphoric anhydride and aluminium chloride by Blanc's method is optically inactive, and so are its salts and esters. The acid prepared by electrolysis is also inactive, and this inactivity is likewise characteristic of isolauronolic acid prepared

from the campholytic acid of electrolysis, as well as of the campholytic acid prepared from isolaunonic acid (this vol., pp. 378, 380). The hydrocarbon isolaunolene,  $C_8H_{14}$ , derived from the hydrobromides of campholytic and isolaunonic acids (this vol., p. 380), is also inactive, which is in accordance with formula IV derived from the Perkin-Bouveault formula of camphoric acid, and in disagreement with formula V, derived from Perkin's later formula for this substance, which still contains an asymmetric carbon atom.

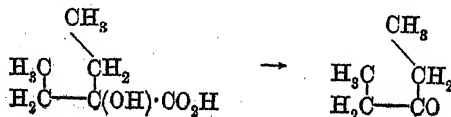


There is absolutely no reason to suppose that racemisation of active compounds takes place during electrolysis, for the allo-campholytic acid produced by the electrolysis of potassium orthoethyl camphorate is strongly active, in accordance with the formula deduced from either the Perkin-Bouveault or the Perkin formula for camphoric acid. An attempt, too, to resolve isolaunonic acid into active constituents by means of cinchonine was made by Blanc, and failed. It must be conceded, therefore, that the inactivity of isolaunonic acid, from whatever source derived, as well as of the related substances, campholytic acid and isolaunolene, affords very strong evidence in favour of the Perkin-Bouveault formula for camphoric acid. It is impossible, either from Perkin's second formula or from Bredt's formula, to derive a formula for isolaunonic acid which shows this substance to be at once an  $\alpha\beta$ -unsaturated acid, and inherently inactive.

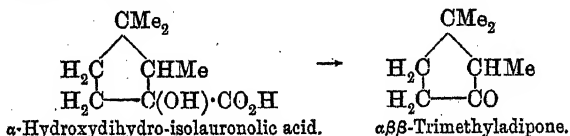
The Perkin-Bouveault formula for camphoric acid has recently received synthetic confirmation from Noyes (*Ber.*, 1900, 33, 54), who, by heating calcium  $\alpha\beta$ -trimethyladipate, prepared the corresponding ketone, thus:



Now, just as diethyl ketone can be produced from diethylhydroxyacetic acid,



so  $\alpha\beta\beta$ -trimethyladipone can be derived from  $\alpha$ -hydroxydihydro-isolauronic acid by oxidation, proving that the latter has the formula given below,

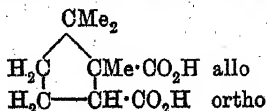


Chemists are agreed, however, that one of the carboxyl groups of camphoric acid is attached to the carbon atom which is united with the solitary methyl group, and the above reactions show that the second carboxyl group is attached to the neighbouring carbon atom. Camphoric acid is therefore a derivative of succinic acid, in accordance with Perkin's first formula, and not a glutaric acid derivative, as Perkin's second formula and Bredt's formula would represent it.

#### *Configuration of the Camphoric Acids.*

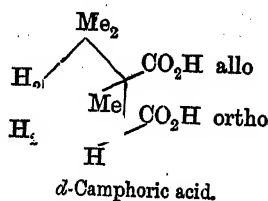
It has been shown (this vol., p. 390) that *d*-camphoric acid and *l*-isocamphoric acid have the same configuration of the allo-asymmetric carbon atom. This circumstance, when taken in conjunction with other well-known facts, enables us to write the configurations of all the camphoric acids on the basis of the Perkin-Bouveault formula.

In the first place, we have to determine which of the carboxyl groups in the formula is to be called the ortho-carboxyl group and which the allo-carboxyl group. This may be readily done by considering the ease with which the respective groups are esterified, and with which the corresponding esters are hydrolysed. One of the carboxyl groups in the formula is attached to a tertiary, and the other to a secondary carbon atom. Now, it is well known that the esters of tertiary acids are much less readily produced and hydrolysed than those of secondary acids. According to the experience of all observers (for example, Friedel, Brühl, and myself) it is a comparatively difficult matter to produce allo-alkyl derivatives and to hydrolyse them after they are obtained (compare this vol., p. 389), whilst the production and hydrolysis of the ortho-camphoric esters can be readily effected. We must therefore give the designation ortho to the secondary asymmetric carbon atom and to the carboxyl group with which it is united, reserving the term allo for the tertiary asymmetric carbon atom and the corresponding carboxyl group, thus:

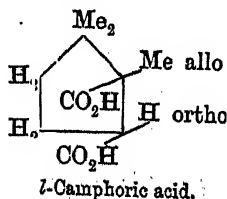


This mode of designation is in entire agreement with the results of electrolysis, the allo-ethyl salts yielding  $\beta\gamma$ -unsaturated acids, and the ortho-ethyl salts yielding  $\alpha\beta$ -unsaturated acids, as would be directly deduced from the formula.

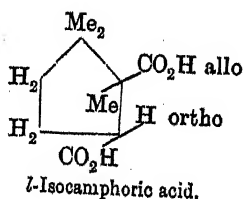
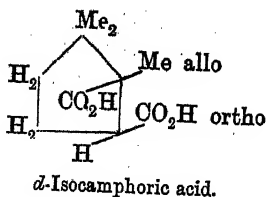
Since camphoric acid and its optical antipode easily yield anhydrides, whilst anhydrides of the isocamphoric acids have never been prepared, we must assume that in the first instance the carboxyl groups are on the same side, and in the second instance on different sides of the ring. If, then, we write the configuration formula of *d*-camphoric acid as follows:



that of *l*-camphoric acid becomes



But since *d*-camphoric acid has the same configuration of the allo-asymmetric carbon atom as *l*-isocamphoric acid, we have for the remaining acids the following formulae.



#### *Dissociation Constants of Camphoric Acid and its Derivatives.*

Ostwald (*Zeit. physikal. Chem.*, 1889, 3, 402) found for camphoric acid the constant  $K = 0.00225$ . On comparing this value with the dissociation constants of the following normal saturated dicarboxylic acids,



Acid.		K.
Malonic .....	$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .....	0.158
Succinic .....	$\text{CO}_2\text{H}\cdot(\text{CH}_2)_2\cdot\text{CO}_2\text{H}$ ...	0.0066
Glutaric.....	$\text{CO}_2\text{H}\cdot(\text{CH}_2)_3\cdot\text{CO}_2\text{H}$ ...	0.0047
Adipic .....	$\text{CO}_2\text{H}\cdot(\text{CH}_2)_4\cdot\text{CO}_2\text{H}$ ...	0.0037
Sebacic .....	$\text{CO}_2\text{H}\cdot(\text{CH}_2)_8\cdot\text{CO}_2\text{H}$ ...	0.0023

we find it to be comparatively small, and Ostwald drew the conclusion that the carboxyl groups in the camphoric acid molecule were probably far apart from each other, seeing that in this series the value of the dissociation constant falls off as the number of carbon atoms between the carboxyl groups increases.

Now, the Perkin-Bouveault formula represents camphoric acid as a succinic acid derivative, whilst according to the formula of Brett and the second formula of Perkin, it is a derivative of glutaric acid. In either case, the dissociation constant is much less than that of the parent substance.

The low value of the dissociation constant of camphoric acid might be accounted for in two ways. In the first place, the formation of a ring might lower the value of the constant. This explanation, however, is invalid, as I have shown (Trans., 1892, 61, 705) that ring formation has little effect on the dissociation constants of acids. In the second place, the replacement of hydrogen atoms of succinic or glutaric acid by hydrocarbon radicles might be the cause of the diminution. At first sight, this explanation appears equally invalid with the first, for the dissociation constants of the alkyl-succinic and alkyl-glutaric acids are, almost without exception, considerably greater than those of the parent acids. For example, for the methyl succinic acids we have

Acid.		K.
Succinic .....	$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .....	0.0066
Methylsuccinic .....	$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ ...	0.0086
Dimethylsuccinic ...	$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ ...	0.0081
Trimethylsuccinic...	$\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ .	0.031
Tetramethylsuccinic	$\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ ...	0.031

In dealing with a case of this nature, it must be borne in mind, however, that the relatively large values of the dicarboxylic acids are chiefly due to the mutual reinforcement of the carboxyl groups, so that the replacement of hydrogen by an alkyl group may act on the constant in two distinct ways: (1) through the influence of the substitution pure and simple, (2) through the influence due to a change effected in the relative position of the carboxyl groups. The nature of these two influences may easily be investigated separately.

If we consider monocarboxylic acids, the second mode of action is obviously excluded, and we can roughly estimate the effect of a pure substitution. For this purpose, we may take acetic acid and some of its simpler derivatives:

Acid.		K.
Acetic .....	$\text{CH}_3 \cdot \text{CO}_2\text{H}$ .....	0.00180
Propionic .....	$\text{CH}_3\text{Me} \cdot \text{CO}_2\text{H}$ .....	0.00134
Isobutyric .....	$\text{CHMe}_2 \cdot \text{CO}_2\text{H}$ .....	0.00162
Trimethylacetic ...	$\text{CMe}_3 \cdot \text{CO}_2\text{H}$ .....	0.00098
Dimethylethylacetic	$\text{CMe}_2\text{Et} \cdot \text{CO}_2\text{H}$ .....	0.00096

For each alkyl derivative, the constant is less than that of acetic acid, the influence being especially marked in the trialkyl derivatives. The same effect may be observed with unsaturated acids, thus:

Acid.		K.
Acrylic .....	$\text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H}$ .....	0.0056
Crotonic .....	$\text{CHMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ .....	0.0020
Isocrotonic .....	" .....	0.0036
Angelical .....	$\text{CHMe} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$ ...	0.0050
Tiglic .....	" .....	0.00096
Methylethylacrylic..	$\text{CHEt} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$ .....	0.00111

When disturbing influences are absent, therefore, it may be said that the substitution of alkyl for hydrogen frequently lowers the constant to one-half, and in some cases to one-fifth the value for the parent acid.

It is thus practically certain that the rise in the dissociation constant, when hydrogen is replaced by alkyl in succinic or glutaric acid, is due to the approximation of the carboxyl groups, and not to the direct influence of the displacement.

From the point of view of stereochemistry, the carbon atoms in open chain saturated compounds must be conceived as possessing a considerable degree of freedom of movement, a freedom with which they, in great measure, part when they form links in a closed chain, or are joined by a double or triple linking. The substitution of alkyl for hydrogen in an unsaturated dicarboxylic acid, or a saturated cyclic dicarboxylic acid, might therefore be expected to show the customary diminution of the dissociation constant, undisturbed by any marked increase due to the secondary effect of approximation of the carboxyl groups. Data for unsaturated dicarboxylic acids are somewhat scanty, but, such as they are, they bear out the preceding deduction. Thus we have (Walden, *Zeit. physikal. Chem.*, 1891, 8, 494):

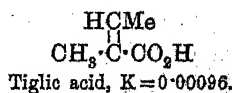
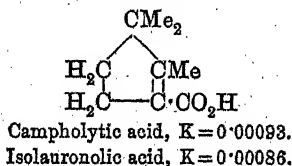
	Acid.	K.		Acid.	K.
Maleic	$\begin{array}{c} \text{H} \text{---} \text{CO}_2\text{H} \\ \text{H} \text{---} \text{CO}_2\text{H} \end{array}$	1.17	Fumaric	$\begin{array}{c} \text{H} \text{---} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \text{---} \text{H} \end{array}$	0.093
Citr- aconic	$\begin{array}{c} \text{Me} \text{---} \text{CO}_2\text{H} \\ \text{H} \text{---} \text{CO}_2\text{H} \end{array}$	0.34	Mes- aconic	$\begin{array}{c} \text{Me} \text{---} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \text{---} \text{H} \end{array}$	0.079
Ethyl- maleic	$\begin{array}{c} \text{Et} \text{---} \text{CO}_2\text{H} \\ \text{H} \text{---} \text{CO}_2\text{H} \end{array}$	0.238	Ethyl- fumaric	$\begin{array}{c} \text{Et} \text{---} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \text{---} \text{H} \end{array}$	0.094

There is little reduction of the dissociation constant in the case of the alkylfumaric acids, but for the alkylmaleic acids it is reduced to less than a third of its value by the introduction of a methyl group, and to a fifth by the introduction of an ethyl group.

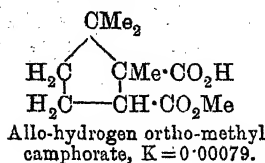
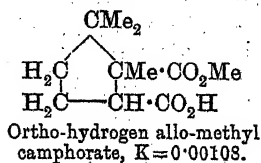
Practically nothing is known of the dissociation constants of saturated cyclic dicarboxylic acids, but in all probability the introduction of alkyl groups instead of hydrogen would exert its primary effect of reducing the constant, as it does in the unsaturated dicarboxylic acids.

These considerations show that, although camphoric acid is regarded as a derivative of glutaric acid, or even of succinic acid, there is in reality nothing abnormal in the small value of its constant, for all chemists agree that in its molecule there remains only one hydrogen atom attached to the carbon atoms with which the carboxyl groups are united.

If the preceding interpretation is correct, monobasic acids derived from camphoric acid should exhibit constants considerably smaller than that of acetic acid, for, in their case, the same influences would be at work to reduce the constant, as in camphoric acid itself. This is, in fact, the case. Thus, for the  $\alpha\beta$ -unsaturated tertiary acids, isolaunonic acid and campholytic acid, we have values which are much less than that of acetic acid, and comparable with that of the  $\alpha\beta$ -unsaturated tertiary acid, tiglic acid :



Again, the constants of the hydrogen methyl camphorates are as follows:



Once more, the very small values appear, and, as we might expect, the constant of the tertiary or allo-carboxylic acid is less than that of the secondary or ortho-carboxylic acid.

The constants of the isocamphoric acids are still less than those of the camphoric acids proper, in accordance with the fact that the former have the *cis*-configuration, and the latter the *cistrans*-configuration. Thus, for *l*-isocamphoric acid we have the constant 0.00160, and for allo-hydrogen ortho-ethyl camphorate the constant 0.00065.

We conclude then from these measurements that the low value of the constant for camphoric acid need not be due to the carboxyl groups being far apart in the molecule, but to the fact that all but one of the hydrogen atoms of the succinic acid, from which, according to the Perkin-Bouveault formula, camphoric acid is derived, are replaced by hydrocarbon groups, which exert their primary effect in lowering the dissociation constant.

The author desires to express his indebtedness for valuable criticism and suggestions to Professor W. H. Perkin, who kindly revised this paper in manuscript.

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### XXXIX.—*The Maximum Pressure of Naphthalene Vapour.*

By RICHARD WILLIAM ALLEN, M.A., University College,  
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THE formation of naphthalene during the carbonisation of coal in gas works is a source of much trouble to gas engineers, for the naphthalene, finding its way into the pipes, forms deposits which obstruct the passage of the gas. The systematic study of the causes and means of prevention of such deposits necessitates an exact knowledge of the amount of naphthalene required to saturate a given volume of any gas at various temperatures and consequently of the maximum pressure of naphthalene vapour at such temperatures. The only measurements of the maximum vapour pressure of naphthalene hitherto carried out are those by Naumann (*Ber.*, 1871, 4, 647) which are as follows:

At 15° vapour pressure = 2 mm.

At 78° vapour pressure = 9 „

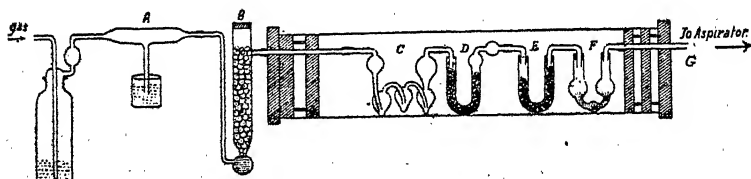
At 100° vapour pressure = 20.5 „

The absence of decimals (other than the 5) suggests that they are only approximations, and they were, in fact, determined in the ordinary barometric vacuum without any special precautions; the tube was jacketed for a few centimetres only below the top of the mercury column, and no method of direct comparison with a standard barometer was employed. Moreover, the value 2 mm. for the vapour pressure at 15° is improbable, for any substance having that vapour pressure at 15° would soon disappear if freely exposed to the air, whereas a small piece of naphthalene so treated shows little diminution in size, even after many weeks. That Naumann was satisfied with an approximation is not to be wondered at, since, except from the point of view of the coal gas industry, a knowledge of the maximum pressure of naphthalene vapour does not appear to be of much importance. Ramsay and Young (*Phil. Trans.*, 1884, Part I, xxxvii, 461) applied the apparatus they devised for measuring the influence of pressure on the temperature of volatilisation of solids to the measurement of the vapour pressures of benzene, water, acetic acid, and camphor, but the preliminary observations they made with naphthalene led to no result, and were abandoned owing to the low vapour pressure of the hydrocarbon (9 mm.) at its melting point (97·6°), and to the want of data regarding its vapour pressure at low temperatures; it may therefore be assumed that the method is inapplicable to naphthalene at the ordinary temperature.

The vapour pressure of naphthalene at the ordinary temperature being very small, the ordinary method of measurement in the barometric vacuum was at first deemed unsuitable. Among other methods, that of evaporation, which has been occasionally employed in the case of liquids, seemed to offer decided advantages. In it, as is well known, a given volume of an indifferent gas at a definite temperature is passed over a weighed quantity of the substance whose vapour pressure is to be measured, and the loss in weight of the latter estimated; this loss represents the weight, and hence the volume, of the vapour required to saturate the given volume of the gas at the given temperature and pressure, and a simple calculation yields the value of the vapour pressure at that temperature. The method is based on the assumption which was proved to be legitimate by the experiments of Regnault and Magnus, that the vapour pressure of a volatile liquid in a space filled with an indifferent gas is very nearly equal to the vapour pressure in a vacuum, and the more nearly is it so the smaller the pressure of the vapour. J. Walker (*Zeit. physikal. Chem.*, 1888, 2, 602) measured the relative vapour pressures of aqueous solutions of various inorganic salts, and Wall and Bredig (*Ber.*, 1889, 22, 1084) those of various alcoholic solutions by this method and obtained very good results. The process being unlimited as regards the length of

time for which the gas is passed, the slowness of the operation, and the volume of the gas employed, it seemed capable of great delicacy and exactness, and hence especially well adapted for measuring the low vapour pressures of such solids as naphthalene. Some pure naphthalene was accordingly first prepared by digesting a commercial sample alternately with sulphuric acid and caustic potash several times and washing repeatedly with water between each digestion; in this way, most of the phenols and hydrocarbons were removed. The purified sample was then three times distilled with steam; finally, it was drained free from water, melted, powdered, and set to dry for several weeks in a large bell jar over concentrated sulphuric acid. It then melted at  $79.6^{\circ}$  and gave only a slight pink coloration on boiling with strong sulphuric acid; hence it might be considered pure. This dry, powdered naphthalene was then filled into light U-tubes, above the powder a little cotton wool was placed to prevent any of it being carried over mechanically, and dry corks, provided with glass outlet tubes, were fitted into the tubes and rendered air-

Fig. 1.



tight with a coating of cement. In order that the temperature of the experiment might be kept perfectly under control, a large zinc water-bath three feet long, two feet six inches high, and two feet three inches wide was constructed. It had six air compartments running lengthwise through it, arranged in two tiers of three each, each compartment being six inches high and four inches wide. The water could circulate freely round each compartment, and was kept well stirred by a large iron stirrer working up and down and driven by a water engine at any desired speed. The temperature of the water was controlled by means of a mercury thermostat, to which was attached a non-atmospheric burner capable of very delicate adjustment. The bath was fitted with a close lid which had three small holes, one in the centre for the rod of the stirrer, and two close together at one end and in the middle line, one being for the thermostat, the other for the thermometers, which were all divided to tenths of a degree. By these means, the temperature could be kept constant throughout the bath to  $0.1^{\circ}$  for 24 hours. Fig. 1 shows the arrangement for one compartment: the gas, entering through the wash-

bottle into the safety tube, A, inserted to measure the pressure in the apparatus and prevent it exceeding that of the atmosphere, was partially dried by passage up a cylinder, B, filled with beads moistened with concentrated sulphuric acid. After being further dried and raised to the temperature of the bath by passage through the sulphuric acid bulb, C, and the calcium chloride tube, D, the gas was passed through the weighed tube of naphthalene, E. In the succeeding sulphuric acid tube, F, most of the naphthalene carried over was re-absorbed and thus prevented from condensing in the tubes outside the bath and blocking them up. The tube G is connected with an aspirator by means of which the gas is drawn through the system of tubes. The several aspirators had slightly different capacities, but as each experiment was concluded the pressure and temperature of the atmosphere were observed, and due correction being also applied for the water vapour saturating the gas in the aspirator, the weight of naphthalene carried over in the given time by 36 litres of dry gas at 15° and 760 mm. pressure was calculated from the observed values. Thus the figures given in the third column of Tables I, II, III, and IV are strictly comparable. The ends of each air compartment were carefully closed, as shown in Fig. 1, by stoppers made of triple layers

TABLE I.

Gas employed. Temp. 30°.	Duration of experiment.	Weight of naphthalene carried over.
Air	2½ hours	0·0318 gram
"	3½ "	0·0319 "
"	4 "	0·0320 "
"	7 "	0·0322 "
"	9½ "	0·0324 "
"	11 "	0·0327 "
"	17 "	0·0330 "
"	30 "	0·0332 "
"	39 "	0·0335 "
"	135 "	0·0340 "
Hydrogen	1½ "	0·0312 "
"	4½ "	0·0313 "
"	6½ "	0·0315 "
"	14 "	0·0330 "
"	24 "	0·0337 "
"	110 "	0·0342 "
Coal gas	3 "	0·0315 "
"	6 "	0·0320 "
"	15 "	0·0322 "
"	20 "	0·0325 "
"	55 "	0·0339 "

of wood, each layer being covered by flannel and separated with cork from the adjoining one. In this way, air currents were prevented, and the temperature in a compartment ensured as being that of the water of the bath. The temperature of the bath having been raised in the first place exactly to  $30^{\circ}$ , and the various tubes arranged as described, the gas was passed at various speeds through the weighed tubes of naphthalene, and the loss in weight of the tubes observed; from this the weight of naphthalene required to saturate 36 litres of dry gas measured at  $15^{\circ}$  and 760 mm. was calculated. It remains to be mentioned that, in addition to air, hydrogen and coal gas were employed in these experiments, as it was deemed better not to rely on results obtained by one gas only: when these gases were employed, the U-tubes of naphthalene were always swept clear of them before weighing by blowing a small quantity (about 50 c.c.) of dry air through them; trial showed that the extra loss of naphthalene due to this precaution was quite negligible. In Table I (p. 403) are given the observed results.

It is noticeable that the weight of naphthalene carried over increases slightly as the rate at which the gas is passed over diminishes. The nature, however, of the gas into which the naphthalene diffuses seems to exercise no influence on the rapidity of the diffusion; the values in Tables II and III confirm this. From the above figures, it would appear that practically complete saturation was attained in the slowest experiments; owing, however, to the obvious difficulty of keeping a large bulk of water at a constant temperature much higher than that of the surrounding air for days at a time, and inasmuch as 97 per cent. saturation was obtained in the 24 and 30 hours experiments, it was decided to limit future experiments to about 24 hours, and allow an extra 3 per cent. on the observed values in order to obtain the true saturation or "limit" value. Tables II, III, and IV contain the results of experiments conducted at other temperatures. As previously, due corrections have been made in each experiment for temperature and pressure, and for the hygrometric state of the gas in the aspirators, the values given being those for 36 litres of dry air at  $15^{\circ}$  and 760 mm. pressure.

TABLE II.

Gas employed. Temp. $45^{\circ}$ .	Duration of experiment.	Weight of naphthalene carried off.
Air	$1\frac{1}{2}$ hours	0.1192 gram
"	$2\frac{1}{2}$ "	0.1222 "
"	$2\frac{3}{4}$ "	0.1224 "
"	5 "	0.1232 "
"	9 "	0.1250 "
"	21 "	0.1260 "



TABLE II.—(continued).

Gas employed. Temp. 45°.	Duration of ex- periment.	Weight of naphthalene carried off.
Hydrogen	1½ hours	0·1194 gram
"	3 "	0·1214 "
"	6 "	0·1236 "
"	8½ "	0·1252 "
"	24 "	0·1272 "
Coal gas	2½ "	0·1204 "
"	5 "	0·1224 "
"	5 "	0·1228 "
"	18 "	0·1260 "
"	22 "	0·1270 "

Limit value = (0·1272 + 3 per cent.) gram.  
= 0·1310 gram.

which is taken to be the true weight of naphthalene required at 45° to saturate 36 litres of dry air measured at 760 mm. and 15°.

TABLE III.

Gas employed. Temp. 60°.	Duration of ex- periment.	Weight of naphthalene carried off.
Air	2½ hours	0·3784 gram
"	5 "	0·4010 "
"	15 "	0·4498 "
Hydrogen	2 "	0·3818 "
"	3½ "	0·3972 "
"	4½ "	0·4048 "
"	15 "	0·4445 "
"	30 "	0·4515 "
Coal gas	1½ "	0·3728 "
"	3½ "	0·4016 "
"	19 "	0·4509 "

Limit value = (0·4515 + 3 per cent.) gram.  
= 0·4650 gram.

TABLE IV.

Temperature of air.	Duration of experiment.	Weight of naphthalene carried off.
15°	2½ hours	0.0165 gram
15	4 "	0.0166 "
15	10 "	0.0168 "
15	93 "	0.0170 "
75	2½ "	1.165 "
75	3 "	1.180 "
75	3½ "	1.191 "

It was found impossible to keep the water in the bath constant at 75° for more than 3—4 hours, hence the limit value for 75° cannot be ascertained with certainty; but assuming that the rate of increase in weight of naphthalene carried over as the length of experiment becomes greater is in the same proportion as at 60°, we may deduce it as follows: Mean weight carried over at 60° in 3½ hours = 0.399 gram — limit assumed = 0.465 gram, or an increase of 17 per cent. Now increase the weight carried over at 75° in 3½ hours, that is, 1.191 grams by 17 per cent., and a limit value of 1.395 grams is obtained.

From these limit values, the vapour pressure of the naphthalene may be easily deduced by means of Ostwald's formula ("Physico-Chemical Measurements," p. 114)

$$p = \frac{62290}{m} \frac{gT}{v} \text{ mm.}$$

where  $g$  = weight in grams of the substance carried off.

$T$  = absolute temperature of room.

$m$  = molecular weight of the body.

$v$  = volume of gas passed over the solid.

Substituting the following values in the above equation, we get the results set forth in Table V.

$g$  = weight of naphthalene carried over given in column 2.

$T = 273 + 15 = 288^\circ$ .

$m = 128$  and  $v = 36000$  c.c.

TABLE V.

Temperature.	Limit weight of naphthalene carried over.	Corresponding vapour pressure.
15°	0.0170 gram	0.066 mm.
30	0.0345 "	0.135 "
45	0.1312 "	0.51 "
60	0.4650 "	1.81 "
75	1.395 "	5.43 "

These values differ so much from those usually given for the vapour pressure of naphthalene, that it was thought that, with due care, they might easily be either confirmed or refuted by the ordinary barometric method. Accordingly, glass tubes  $\frac{5}{8}$ -in. in diameter and 3 ft. long were taken, thoroughly cleaned, and drawn out at one end to a fine capillary thread, so that the free end might be connected with the mercury joint of a Sprengel pump. Each tube was then strongly heated to expel all moisture, the capillary end connected with the pump, and the other end dipped into hot, freshly distilled mercury, which was then slowly drawn up by means of the pump. As the mercury rose, it was boiled by means of a large Bunsen burner, finally the mercury was boiled throughout its whole length, and the tubes lowered into the bath till the mercury rose well into the capillary thread, when the tubes were sealed off with the blow-pipe. After several attempts, two tubes were obtained in which the residual air could, with difficulty, be distinguished on inclining the tubes. The heights of the mercury in the two tubes, as read off by the cathetometer (which read with great accuracy to 0.01 mm.), were exactly the same. Having thus obtained two perfect barometer tubes, a small glass bulb blown in a capillary thread was filled with pure melted naphthalene by suction with a pump, and the ends sealed off when the naphthalene had solidified. Before passing this bulb up into one of the barometer tubes, it was cleaned and dried, and the mercury in the trough warmed so as to prevent the introduction of moisture. Notwithstanding all precautions, a small quantity of air was introduced with the bulb, and the mercury stood 1.86 mm. lower than it did in the standard barometer. The naphthalene bulb was then burst by warming the top of the mercury column, and the tube inclined, and clamped in that position, so that, on cooling, the naphthalene with the bulb attached to it solidified in the top of the tube, and so did not interfere with the readings. The two barometers were now lashed together, and delicate thermometers, divided to tenths of a degree, fastened between them. To ascertain whether the depression in the experimental tube, due to the air admitted, amounted exactly to 1.86 mm. at 15° or whether an additional small quantity of air had been enclosed in the bulb with the naphthalene, the two tubes were enclosed in a case with plate glass windows, and surrounded with a freezing mixture. After the temperature had remained constant at -18° for 20 minutes, the heights in the two columns were taken. At the temperature -18°, it was assumed that the naphthalene had practically no vapour pressure; on this assumption the difference of level of the mercury columns A and B. was due solely to the air in B. The readings were as follows:

Barometer = 759.6 mm.

Height of the column in A = 448.04 mm.

" " " B = 446.36 "

Difference.....  $1.68 \text{ mm.} = 1.68 \times (1 + 18 \times 0.000179)$   
 $= 1.68 \text{ mm. of mercury at } 0^\circ.$

A simple calculation shows that the air, which exerts a pressure of 1.68 mm. at  $-18^\circ$  and 759.6 mm., will exert a pressure of 1.90 mm. at  $15^\circ$  and 760 mm. Before bursting the bulb, the difference of level was 1.86 mm., so that the air that had been enclosed with the naphthalene was only sufficient to produce a depression of 0.04 mm. at  $15^\circ$ . The freezing mixture having been removed, and the tubes allowed to take the temperature of the air, they were surrounded with the melting ice. After the temperature of the air space above the ice had remained constant at zero for a considerable time, new readings were taken as follows:

Temperature =  $0^\circ$  Barometer = 759.9 mm.

Height of mercury in column A = 448.34 mm.

" " " B = 446.53 "

Difference..... 1.81 "

of which difference  $\frac{1.68 \times 273 \times 760}{(273 - 18) \times 759.9}$  mm., or 1.80 mm., are due to

air, hence the true vapour pressure at  $0^\circ = 0.01 \text{ mm.}$  The case was now removed and next day, after the temperature had been constant at  $15.6^\circ$  for an hour, fresh readings were taken as follows:

Barometer = 758.6 mm.

Height of mercury column in A = 439.08 mm.

" " " B = 437.10 "

Difference..... 1.98 "

Subtract  $\frac{1.80 \times (273 + 15.6) \times 760}{273 \times 558.6}$  mm. or 1.90 mm. for air and

vapour pressure at  $15.6 = 0.08 \text{ mm. of mercury at } 0^\circ.$  The value found by the "evaporation method," 0.068 mm. at  $15^\circ$ , agrees well with this. In order to obtain values at other temperatures, the tubes were jacketed with a Hofmann's density tube, and the vapours of the following substances introduced: ether, carbon disulphide, chloroform, alcohol, benzene, water, acetic acid, isoamyl alcohol, boiling at  $39^\circ$ ,  $46.8^\circ$ ,  $61.8^\circ$ ,  $78.4^\circ$ ,  $80.4^\circ$ ,  $100^\circ$ ,  $116^\circ$ , and  $130^\circ$  respectively, as indicated by the thermometers. The following results were now obtained:



Benzene, b. p.  $80.4^{\circ}$ . Barometer = 760 mm.

Height of mercury column in A = 459.82 mm.

"	"	"	B = 449.84	"
				"

	Difference =	9.98	"
--	--------------	------	---

Depression due to air,

$$= \frac{1.80 \times (273 + 80.4)}{273} = 2.33 \quad "$$

Hence vapour pressure at  $80.4^{\circ}$  = 7.65    "    of mercury at  $80.4^{\circ}$ .= 7.54    "    of mercury at  $0^{\circ}$ .Water, b. p.  $100^{\circ}$ . Barometer = 759 mm.

Height of mercury column in A = 459.12 mm.

"	"	"	B = 437.84	"
				"

	Difference =	21.28	"
--	--------------	-------	---

Depression due to air,

$$= \frac{1.80 \times (273 + 100) \times 760}{273 \times 759} = 2.44 \quad "$$

Hence vapour pressure at  $100^{\circ}$  = 18.84    "    of mercury at  $100^{\circ}$ .= 18.50    "    of mercury at  $0^{\circ}$ .Acetic acid, b. p.  $118^{\circ}$ . Barometer = 760.4 mm.

Height of mercury column in A = 460.86 mm.

"	"	"	B = 420.60	"
				"

	Difference =	40.26	"
--	--------------	-------	---

Depression due to air

$$= \frac{1.80 \times (273 + 116) \times 760}{273 \times 760.4} = 2.58 \quad "$$

Hence vapour pressure at  $118^{\circ}$  = 37.68    "    of mercury at  $118^{\circ}$ .= 36.87    "    of mercury at  $0^{\circ}$ .Isoamyl alcohol, b. p.  $130^{\circ}$ . Barometer = 761.6 mm.

Height of mercury column in A = 462.66 mm.

"	"	"	B = 396.50	"
				"

	Difference =	66.16	"
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Depression due to air

$$= \frac{1.80 \times 273 + 138 \times 760}{273 \times 761.6} = 2.70 \quad "$$

Hence vapour pressure at  $130^{\circ}$  = 63.46    "    of mercury at  $130^{\circ}$ .= 61.95    "    of mercury at  $0^{\circ}$ .

In Table VI are set out the results thus obtained by the barometric method.

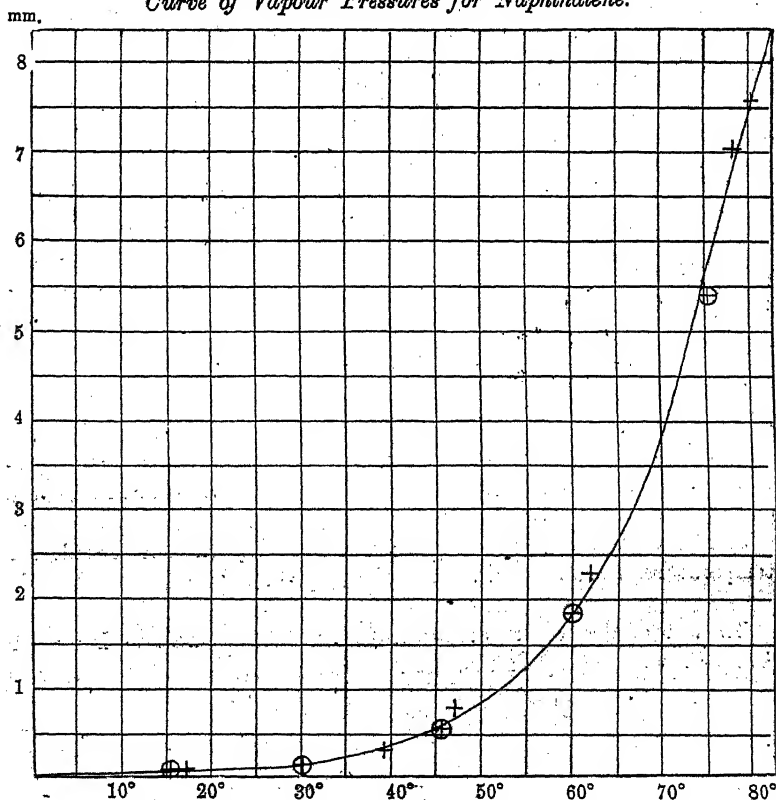
TABLE VI.

Temperature.	Corresponding vapour pressure.	Temperature.	Corresponding vapour pressure.
0°	0.01 mm.	78.4°	7.01 mm.
15.6	0.08 "	80.4	7.54 "
39	0.30 "	100	18.50 "
46.8	0.73 "	116	36.87 "
61.8	2.26 "	130	61.95 "

The values obtained by the two methods were then plotted out and a curve constructed.

FIG. 2.

*Curve of Vapour Pressures for Naphthalene.*



Values obtained by evaporation method are marked ⊕.  
Values obtained by barometric method are marked +.

The agreement between the two sets of values is very close; from the curve shown on a reduced scale in Fig. 2, the maximum vapour pressures corresponding to every 5° were deduced. These values are given in Table VII.

TABLE VII.

Temperature.	Corresponding vapour pressure.	Temperature.	Corresponding vapour pressure.
0°	0.022 mm.	70°	3.95 mm.
5	0.034 "	75	5.43 "
10	0.047 "	80	7.4 "
15	0.062 "	85	9.8 "
20	0.080 "	90	12.6 "
25	0.103 "	95	15.5 "
30	0.135 "	100	18.5 "
35	0.21 "	105	22.4 "
40	0.32 "	110	27.3 "
45	0.51 "	115	32.4 "
50	0.81 "	120	40.2 "
55	1.26 "	125	49.8 "
60	1.83 "	130	61.9 "
65	2.65 "		

In conclusion, attention may be drawn to the following points:

1. The great advantages that the "evaporation method" has over other methods in measurements of the low vapour pressure of solids at moderate temperatures, both in regard to accuracy and ease of manipulation.

2. The rate of evaporation of the naphthalene into the three gases, hydrogen, air, and coal gas is the same in each case, being independent of the nature of the gas. This is confirmed by other experiments, in which carbon dioxide, acetylene, marsh gas, and air containing the vapours of ether, carbon disulphide, benzene, chloroform, or ethyl alcohol, in quantities insufficient for saturation, were employed instead of the above three gases.

3. The very much lower vapour pressure of naphthalene at moderate temperatures than has been hitherto accepted.

The author desires to acknowledge his indebtedness to Professor F. D. Brown for help and advice received during the progress of this investigation.



# *XL.—The Maximum Pressure of Camphor Vapour.*

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IN the preceding paper were recorded the results of some experiments on the maximum vapour pressure of naphthalene at moderate temperatures both by the "evaporation" and "barometric" methods, and the values found by the two methods were seen to be identical. The following experiments with camphor were made with the view of further testing the accuracy of the "evaporation method," and as the numbers obtained differ somewhat from those usually accepted, it seemed desirable to communicate them to the Society. Camphor was selected for experiment, because its maximum vapour pressure at moderate temperatures was as uncertain as that of naphthalene, as may be seen from the adjoined table, which contains the two sets of values found by Ramsay and Young (*Phil. Trans.*, 1884, Part I, 45), the first set measured in the barometric vacuum, the second in the apparatus they devised and described in the paper quoted.

TABLE I.

Temperature.	Vapour pressure found in barometric vacuum.	Vapour pressure found by Ramsay and Young.
20°	1 mm.	
35	1·8 „	
41·2		1·7 mm.
62·4	6·4 „	
68·9		7·2 „
78·4	9·5 „	
92·4		15·4 „
100	22·6 „	
101		27·2 „

The agreement between the two sets of values is by no means perfect, as is very evident when they are plotted out as curves.

The camphor for my experiments was purified by sublimation, and the light, feathery crystals thus obtained were dried over strong sulphuric acid. The apparatus and method of working were the same as with naphthalene.

The results obtained by the "evaporation method" are given in table II (p. 414).

TABLE II.

Temperature.	Duration of experiment.	Weight of camphor carried over.	Limit value.
15.6° "	1 hour 3 hours	0.0355 gram 0.0357 "	} 0.038 gram
35° " " "	1 hour 1½ hours 3 " 4½ "	0.0930 " 0.0933 " 0.0942 " 0.0950 "	} 0.101 "
45° "	3 " 6 "	0.2600 " 0.2616 "	} 0.278 "
49° "	1½ hours 3 "	0.345 " 0.350 "	} 0.374 "
75° " "	3½ " 5 " 7 "	1.717 " 1.738 " 1.748 "	} 2.01 "

These results give for the vapour pressure of camphor at the several temperatures as calculated by Ostwald's formula ("Physico-Chemical Measurements," 114)

$$\text{vapour pressure} = \frac{62290 gT}{m v} \text{ mm.}$$

the following values (Table III).

TABLE III.

Temperature.	Weight of camphor carried over.	Corresponding vapour pressure.
15.6°	0.038 gram	0.14 mm.
35.0	0.101 "	0.33 "
45.0	0.278 "	0.91 "
49.0	0.374 "	1.23 "
75.0	2.01 grams	6.59 "

The values found by the evaporation method were now confirmed, as in the case of naphthalene, by the "barometric method"; the method of working, being exactly the same as before, need not be described again. As in the case of naphthalene, it was found impossible to prevent a minute quantity of air passing up the tube; the depression of the mercurial column due to it was determined and allowed for in the same way as before.

In table IV are given the results now obtained by the "barometric method."

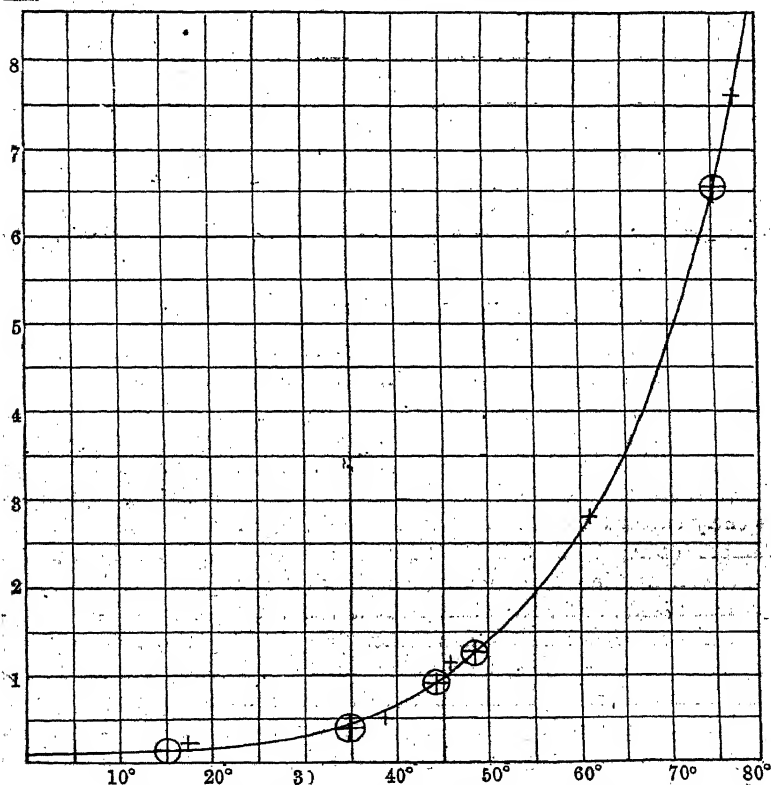
TABLE IV.

Temperature.	Corresponding vapour pressure.
17.0°	0.15 mm.
39.0	0.53 "
46.6	1.11 "
61.8	2.82 "
78.2	7.62 "

The numbers found by the two methods when plotted out were all found to lie exactly on the same curve, and consequently are identical at the same temperatures.

*Curve of Vapour Pressures for Camphor.*

mm.



Values obtained by evaporation method are marked ⊕.

Values obtained by barometric method are marked +.

The exact concordance of the two sets of results is a further proof of the value of the "evaporation" method in the measurement of very low vapour pressures.

In the following table are given the maximum vapour pressures of camphor for every five degrees from 0° to 80° as read off from a curve where 20 divisions = 1mm. of vapour pressure.

TABLE V.

Temperature.	Corresponding vapour pressure.	Temperature.	Corresponding vapour pressure.
0°	0·06 mm.	45°	0·90 mm.
5	0·08 "	50	1·30 "
10	0·10 "	55	1·85 "
15	0·12 "	60	2·55 "
20	0·15 "	65	3·40 "
25	0·19 "	70	4·60 "
30	0·26 "	75	6·50 "
35	0·38 "	80	9·15 "
40	0·60 "		

## XLI.—*Apiin and Apigenin. Part II. Note on Vitexin.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

THE reactions of apigenin (Trans., 1897, 71, 805; 1898, 73, 666), the yellow colouring matter of parsley (*Apium petroselinum*), have indicated that it is most probably a trihydroxyflavone. Its properties markedly resemble those of chrysin present in poplar buds, and the dihydroxyflavone constitution assigned to the latter compound by von Kostanecki (Ber., 1893, 26, 2901) has received full proof from the synthesis recently effected by this author in conjunction with Emilewicz and Tambor (Ber., 1899, 32, 13, 2448). In assigning to apigenin the above constitution, one doubtful point exists as regards its behaviour towards fused alkali, for whereas at a lower temperature *p*-hydroxyacetophenone is formed, a more energetic action gives, not only the expected *p*-hydroxybenzoic acid, but also protocatechuic acid. On the other hand, the methyl and ethyl ethers of this colouring matter yield, by means of alcoholic potash, the corresponding ethers of *p*-hydroxybenzoic acid only, suggesting that the formation of protocatechuic acid is due rather to a process of oxidation than to the presence of a catechol nucleus in the substance. Desiring to obtain further in-

formation upon this point, the behaviour of apigenin with nitric acid has been studied; this was also interesting as tracing further its analogy to chrysin, which also yields a mononitro-derivative (Piccard, *Ber.*, 1873, 6, 884), and might also elucidate the constitution of vitexin (*Trans.*, 1898, 73, 1026). The last colouring matter is apparently very closely related to apigenin, for not only does it yield the same decomposition products, but forms with nitric acid a substance,  $C_{15}H_6O_5(NO_2)_4$ , having the composition of a tetranitroapigenin.

#### EXPERIMENTAL.

##### *Action of Nitric Acid on Apigenin.*

The crude material for these experiments was the apiin prepared by Merck of Darmstadt, and this was converted into apigenin by the method previously described (*loc. cit.*).

Three grams of finely powdered apigenin were added to a solution of 12 grams of nitric acid of sp. gr. 1.42 in 60 c.c. of water, and the mixture digested at the boiling point for 20 minutes. A portion of the colouring matter was thus decomposed with formation of a pale yellow liquid and that remaining undissolved had a semigelatinous appearance. The latter, which when collected and dried, weighed 1.7 grams, was extracted with boiling alcohol, the extract evaporated to a small bulk and cooled, a gelatinous precipitate thus separating; this on gentle heating became more granular, and was then collected while hot and washed with alcohol. A concentrated solution of the product in hot nitrobenzene, when treated drop by drop with acetic acid, deposited crystals which were collected and washed.

0.1130 gave 0.2358  $CO_2$  and 0.0341  $H_2O$ .  $C=56.91$ ;  $H=3.35$ .

0.1204 „ 5.2 c.c. nitrogen at  $23^\circ$  and 750 mm.  $N=4.80$ .

0.1150 „ 4.9 „ „ „  $21^\circ$  „ 752 „  $N=4.79$ .

$C_{15}H_6O_7N$  requires  $C=57.14$ ;  $H=2.86$ ;  $N=4.44$  per cent.

*Mononitroapigenin*,  $C_{15}H_6O_5 \cdot NO_2$ , forms minute, orange-yellow, prismatic needles, melting with decomposition at about  $302^\circ$  when rapidly heated. Dilute alkalis dissolve it with an orange coloration, but with concentrated solutions a sparingly soluble orange-red salt is formed. As is to be expected, the dyeing power of mononitroapigenin is slightly stronger, and the resulting shades of a more orange character than those given by apigenin itself.

On evaporation to a small bulk, the dilute nitric acid liquid obtained during the preparation of this compound deposited crystals which were collected, washed with water, and purified by recrystallisation from dilute alcohol. It formed colourless leaflets melting at  $235-236^\circ$ , was identified as *m-dinitro-p-hydroxybenzoic acid* by the preparation

of its ethyl salt, which was obtained as colourless needles melting at 86—88°.

When vitexin (*loc. cit.*) is submitted to the prolonged action of dilute nitric acid, the compound  $C_{15}H_6O_5(NO_2)_4$  is produced, but although numerous experiments were carried out, a similar substance could not be prepared from apigenin in this manner. More energetic methods were therefore employed.

Apigenin, in quantities of 1 gram suspended in 5 c.c. of acetic acid, was treated drop by drop with about 4 c.c. of nitric acid of sp. gr. 1.42, the mixture being heated after each addition and allowed to stand until the action had moderated. The reddish-brown liquid at first produced became gradually paler and ultimately a trace of a crystalline powder separated; from this, the acid liquid was decanted, the residue washed with hot acetic acid, digested with a little nitric acid, and recrystallised by adding alcohol to its solution in hot nitrobenzene. The yield approximated to 5 per cent. of the apigenin employed.

0.1089 gave 0.1780  $CO_2$  and 0.0295  $H_2O$ . C = 44.56; H = 3.00.

0.0906 „ 8.4 c.c. nitrogen at 25° and 764 mm. N = 10.39.

0.1150 „ 10.8 „ „ 24° „ 763 „ N = 10.55.

$C_{15}H_7O_{11}N_8$  requires C = 44.44; H = 1.73; N = 10.37 per cent.

The abnormal percentage of hydrogen recorded in the above analysis was due to the sudden decomposition of the substance, some nitrous fumes thus passing to the sulphuric acid employed for the absorption of the water.

*Trinitroapigenin* (a),  $C_{15}H_7O_5(NO_2)_3$ , forms minute, glistening, yellow needles, sparingly soluble in the usual solvents, and when rapidly heated melts with decomposition at about 296°. In its reactions with alkaline solutions, it behaves like the mononitro-compound, but its dyeing properties are stronger and the shades produced of a more orange character. Subsequent experiments showed that a larger yield could be obtained, if in place of apigenin the crude mononitro-derivative is nitrated as in the manner just described. Thus 3 grams of mononitroapigenin gave 0.6 gram of the trinitro-compound or 10 per cent. on the weight of the apigenin first employed.

No higher nitro-derivative could be prepared by digesting trinitroapigenin (a) with boiling nitric acid of sp. gr. 1.42. It was thus slowly decomposed, and a sample of undissolved substance collected during the reaction was evidently unchanged trinitroapigenin, as analysis gave 10.67 per cent. of nitrogen. It is more readily attacked by nitric acid of sp. gr. 1.54, and the solution on evaporation and treatment with water deposited crystals which, after purification, melted at 118—121°, and had the properties of *picric acid*.

A preliminary study of the action of nitric acid of sp. gr. 1.54 was described in the former communication (*loc. cit.*), but the crystalline product was too small in quantity for examination. A slight modification of the method, however, gave better results. Apigenin was added to cold nitric acid of sp. gr. 1.54 until the brown solution deposited a viscous mass, due to the dilution of the acid by the water produced in the reaction. This was redissolved by the addition of a little fresh acid, and, on gently warming, a crystalline product now separated; this was poured into a large volume of water, digested at the boiling point for a few minutes, and the insoluble residue then collected, extracted two or three times with boiling alcohol, and purified by adding alcohol to its solution in hot nitrobenzene.

0.1126 gave 0.1830  $\text{CO}_2$  and 0.0151  $\text{H}_2\text{O}$ .  $\text{C} = 44.32$ ;  $\text{H} = 1.49$ .

0.1033 „ 9.6 c.c. nitrogen at  $18^\circ$  and 742 mm.  $\text{N} = 10.47$ .

$\text{C}_{15}\text{H}_7\text{O}_{11}\text{N}_3$  requires  $\text{C} = 44.44$ ;  $\text{H} = 1.73$ ;  $\text{N} = 10.37$  per cent.

It forms glistening, orange-yellow leaflets, considerably larger than the crystals of the nitro-derivatives just described, and when heated, sinters at about  $240^\circ$ , and melts, with decomposition, at  $245\text{--}246^\circ$ . It is sparingly soluble in the usual solvents, yields, with alkalis, sparingly soluble salts, and on mordanted calico produces shades similar to those obtained with trinitroapigenin (*a*) melting at  $296^\circ$ . The results indicate that this is a second trinitro-compound, which may be called *trinitroapigenin* (*b*), and its identity was rendered certain by the examination of distinct preparations.

The fact that apigenin yields two trinitro-derivatives indicated that it should form a tetranitro-compound, and with the object of preparing such a substance, a mixture of nitric and sulphuric acids was now employed. After numerous experiments, the following method was adopted. Apigenin (1 gram) was added, in small portions at a time, with frequent stirring, to a mixture of 12 c.c. nitric acid of sp. gr. 1.54 and 12 c.c. of sulphuric acid. After standing for 15 minutes without further cooling, the mixture had become somewhat warm; it was then poured into 750 c.c. of boiling water, the resulting opaque liquid being rapidly strained through calico to remove a trace of resinous substance. The filtrate, on digestion at the boiling point, gradually deposited minute, orange-brown needles, which were collected, washed with water, and finally with alcohol, to remove a brown impurity. The product was dissolved in a little hot nitrobenzene, alcohol added to the solution, and the crystals which separated recrystallised in a similar manner. The yield was approximately 0.2 gram.

0.1182 gave 0.1732  $\text{CO}_2$  and 0.0168  $\text{H}_2\text{O}$ .  $\text{C} = 39.95$ ;  $\text{H} = 1.58$ .

0.1111 „ 12.3 c.c. nitrogen at  $21^\circ$  and 760 mm.  $\text{N} = 12.60$ .

0.1068 „ 11.7 „ „  $21^\circ$  „ 758 „  $\text{N} = 12.44$ .

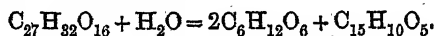
$\text{C}_{15}\text{H}_6\text{O}_{13}\text{N}_4$  require  $\text{C} = 40.00$ ;  $\text{H} = 1.35$ ;  $\text{N} = 12.44$  per cent.

*Tetranitroapigenin*,  $C_{15}H_6O_5(NO_2)_4$ , forms almost colourless needles which rapidly become yellow in the air, and melt, with decomposition, at  $243-244^\circ$ . It is sparingly soluble in the usual solvents, and does not dissolve in alkaline solutions, orange-red, insoluble salts being thus formed. If its solution in hot nitrobenzene is diluted with benzene, crystals containing nitrobenzene separate, which show signs of melting at  $150^\circ$ , owing to its liberation. It dyes mordanted calico similarly to the trinitroapigenins.

In its general reactions, this compound is thus identical with the substance,  $C_{15}H_6O_5(NO_2)_4$ , previously obtained from vitexin (*loc. cit.*). The melting point of this compound is given as  $239-241^\circ$ , but this slight difference is of little importance, for the very meagre yield of the substance from vitexin (2.5 per cent.) did not permit of a fuller purification than that recorded in the paper. The similarity of the melting points of tetranitroapigenin and trinitroapigenin (b) is remarkable.

#### *Action of Nitric Acid on Apiin.*

Apiin,  $C_{27}H_{32}O_{16}$ , is the glucoside of apigenin, and its decomposition acids can be represented as follows:



Gerichten (*Ber.*, 1876, 9, 1124) did not study the action of nitric acid on apigenin, but obtained from apiin with this reagent picric and oxalic acids.

To avoid the tedious operations involved in the conversion of apiin into apigenin which require at least 3 days, it seemed possible that dilute nitric acid would decompose the glucoside into apigenin, which would become simultaneously nitrated. Addition of nitric acid to a boiling aqueous solution of apiin caused the gradual separation of a yellowish-white, gelatinous precipitate, but this, although containing nitrogen, had not the properties of any of the nitroapigenins. The substance prepared in this manner was difficult to manipulate, and this suggested the nitration of apiin in the presence of boiling 60 per cent. acetic acid. In this case, although the apiin did not appear to dissolve, a brisk reaction ensued, and when this had moderated the mixture was diluted with acetic acid and the insoluble residue then collected and washed first with acetic acid and then with alcohol. As analysis showed the presence of 3.35 per cent. of nitrogen, intermediate between that required for a nitroapiin ( $N=2.13$  per cent.) and a nitroapigenin ( $N=4.44$  per cent.), it appeared to be insufficiently nitrated, but a second digestion with boiling nitric and acetic acids produced no alteration in this respect. As other preparations gave similar results, it became evident that a distinct compound is formed in this manner.



0.1245 gave 0.2338 CO<sub>2</sub> and 0.0497 H<sub>2</sub>O. C=51.21; H=4.43.

0.1188 „ 0.2216 CO<sub>2</sub> „ 0.0500 H<sub>2</sub>O. C=50.87; H=4.67.

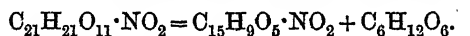
0.1427 „ 4.2 c.c. nitrogen at 24° and 766 mm. N=3.27.

C<sub>21</sub>H<sub>21</sub>O<sub>13</sub>N requires C=50.91; H=4.24; N=2.83 per cent.

It is a pale yellow, crystalline powder melting at 254—255° when slowly heated, sparingly soluble in the usual solvents, soluble in dilute alkalis with a yellow coloration. It dyes mordanted calico analogously to mononitroapigenin. The yield in [one operation was 33 per cent. by weight of the apiin employed. To determine if this substance was a nitro-glucoside, it was digested for 10 hours with dilute hydrochloric acid. The main bulk of the product, previously insoluble, now dissolved in boiling alcohol, and from this solution, by evaporation, a granular, yellow precipitate could be obtained, which crystallised from a mixture of nitrobenzene and alcohol in minute, orange-yellow needles. Its properties and the following analysis proved its identity with the mononitroapigenin above described.

0.1125 gave 4.75 c.c. nitrogen at 21° and 755 mm. N=4.77 per cent.

The action of nitric acid upon apiin consists, therefore, in the removal of one molecular proportion of glucose, and the formation of the nitro-compound of a *new glucoside of apigenin*. It is remarkable, however, that the second glucose molecule cannot be removed by the prolonged action of nitric acid, and that the only change is one of slow but complete decomposition, *m*-dinitro-*p*-hydroxybenzoic acid being recognised as the main product. As shown above, dilute hydrochloric acid effects this change, which occurs probably as follows:

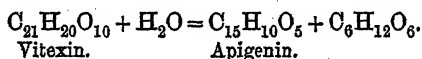


It is proposed to call this substance *nitroapigetrin*, as it is derived from the new glucoside *apigetrin*, which differs from apigenin in containing but one glucose residue.

In the previous communication, it was pointed out that, in order to obtain an apigenin free from glucose, it is necessary to digest apiin for 20 hours with dilute acid. In the light of the above result, it seemed possible that apigetrin might be prepared from apiin by a gentle decomposition with acid, but experiments in this direction yielded in each case a product containing apigenin. It seems, therefore, that the difficulties encountered in preparing pure apigenin are mechanical rather than chemical, and that the semi-gelatinous precipitate of the colouring matter which is first produced, being saturated with the glucoside solution, protects this to a considerable extent from the action of the acid,

*Constitution of Vitexin.*

The identity of the decomposition products (phloroglucinol, *p*-hydroxyacetophenone, and dinitro-*p*-hydroxybenzoic acid) and the similarity of the dyeing properties of vitexin and apigenin, led to the opinion that the constitution of the former might be represented by that of the latter with a side chain attached (Trans., 1898, '73, 1030). As there is now little doubt of the identity of tetranitroapigenin with the compound  $C_{15}H_6O_5(NO_2)_4$ , derived from vitexin, the reasonableness of this view is evident. In considering the constitution of vitexin, to which the provisional formula  $C_{15}H_9O_2(OH)_5$  was assigned, the number of hydroxyl groups is remarkable. These are not fully accounted for by its decomposition products, or expressed in its feeble dyeing properties, and as the apigenin complex it contains has only three hydroxyl groups, it is evident that the molecular weight is higher than that implied above, and that the side chain or residue of the molecule must consequently be rich in hydroxyl. These considerations have led to the suggestion that vitexin is probably a *very stable glucoside of apigenin* represented by the formula  $C_{21}H_{20}O_{10}$  (C=58.33; H=4.62 per cent.), thus:



This conclusion is in harmony with the mean of the previous analytical results (C=58.58; H=4.46 per cent.). Previous figures indicate that this compound contains seven hydroxyl groups, for the yield of vitexin from its acetyl derivative,  $C_{21}H_{18}O_{10}(C_2H_3O)_7$ , was 57.30 per cent.; calculated, 57.96.

A minor point is the dull olive coloration which a sulphuric acid solution of vitexin develops on heating, for this reaction is abnormal and not possessed by colouring matters of the apigenin type. On the above theory, this would be caused by the partial carbonisation of the sugar group, and it is interesting to note that quercetrin, the glucoside of quercetin, gives in this way a somewhat similar coloration. The insolubility of vitexin and its stable nature are at first sight opposed to the above view, for most glucosides are soluble in hot water or alcohol, and readily decomposed by acid. Curiously enough, the former property is possessed by the nitroapigetrin described in this paper, which, although very sparingly soluble, is a glucoside, and the latter by fastin, the glucoside of fisetin (Schmid, *Ber.*, 1886, 19, 1753). Should vitexin possess the constitution of a glucoside, it is probable, in view of its peculiar properties, that the method of attachment of the glucose to the rest of the molecule differs from that usually considered to exist in the ordinary type of these compounds. In a

previous communication, scoparin (Proc., 1899, 15, 123) was shown to have properties in harmony with a *methoxyvitexin*, and this, if containing a sugar group, should thus be a *glucoside of a luteolin monomethyl ether*. Although its stability, as is the case with vitexin, has not allowed of direct evidence on this point, the results at present obtained appear to coincide with this view. A continuation of the work on scoparin and vitexin is now in progress.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant which has in part been used for the expenses of this investigation.

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XLII.—*Yellow Colouring Principles contained in Various Tannin Matters. Part VII. Arctostaphylos Uva ursi, Hamatoxylon Campeachianum, Rhus Metopium Myrica Gale, Coriaria myrtifolia, and Robinia pseudacacia.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

THIS paper embodies the results which have been obtained from time to time during the past eighteen months in continuation of the investigation of the colouring matters associated with various tannins in plants (Trans., 1896, 69, 1289, 1299, 1303,; 1897, 71, 1131, 1194; 1898, 73, 374, 1016). The selection of each plant was suggested by some point of interest in connection with the tannin or colouring matter which a preliminary investigation indicated to be present, whereas the main work was undertaken to determine whether any general relationship exists between the tannin and colouring matter so frequently occurring together (Trans., 1897, 71, 1138).

In the earlier stages of this work, a relationship was noticed between the tannin and colouring matter co-existing in the plants which had been studied (Trans., 1897, 71, 1138), as both contained a similar nucleus. The exceptions brought to light during further investigation, however, are too numerous to allow of a rule being laid down on this point, although such a relationship is more usual than otherwise. It is probable that in some instances the plants contain both catechol and pyrogallol tannins, as is the case with the *Quebracho Colorado* (Trans.,

1896, 69, 1306), and that some exceptions are only apparent. Such a mixture of tannins, however, does not occur in the *Coriaria myrtifolia* described below, as this contains only gallotannin, and it is evident that this substance and the co-existing quercetin do not possess similar nuclei. It is interesting to note that myricetin as yet is only known to be present in plants which also contain a gallotannin.

*Arctostaphylos Uva ursi.*

The *Arctostaphylos Uva ursi*, or bearberry, is found in Great Britain and throughout Northern Europe. The whole plant is astringent and has been employed for tanning leather. It contains arbutin (Kawalier, *Annalen*, 1852, 84, 356), ericolin (Kawalier, *Jahresb.*, 1852, 685), and gallotannic acid (B. de Graffe, *Amer. J. Pharm.*, 1896, 68, 313). In the present investigation, the leaves only were employed and were obtained by purchase from Merck of Darmstadt.

The yellow colouring matter was isolated by the method described in the case of *Rhus Coriaria* (Trans., 1896, 69, 1299). The crude product obtained in this manner was a mixture of the colouring matter with ellagic and gallic acid, the latter being derived from the gallotannin by the action of the acid employed in the operation. After washing with water, the residue was extracted with alcohol, and the ellagic acid which remained undissolved was identified by its dyeing properties and characteristic reaction with nitric and nitrous acids (Griessmayer, *Annalen*, 1871, 160, 55).

The alcoholic extract was evaporated to a small bulk, diluted with boiling water, and the precipitated colouring matter collected and crystallised from dilute alcohol. The yield was approximately 0.3 per cent.

0.0972 gave 0.2110  $\text{CO}_2$  and 0.0313  $\text{H}_2\text{O}$ .  $\text{C} = 59.20$ ;  $\text{H} = 3.57$ .

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires  $\text{C} = 59.60$ ;  $\text{H} = 3.31$  per cent.

The acetyl compound,  $\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_5\text{O})_5$ , obtained as colourless needles, melted at 190–192°.

0.1153 gave 0.2416  $\text{CO}_2$  and 0.0410  $\text{H}_2\text{O}$ .  $\text{C} = 58.21$ ;  $\text{H} = 3.95$ .

$\text{C}_{25}\text{H}_{20}\text{O}_{12}$  requires  $\text{C} = 58.59$ ;  $\text{H} = 3.90$  per cent.

Fusion of the colouring matter with alkali gave phloroglucinol and protocatechuic acid; the latter, however, did not melt quite sharply, and appeared to contain a trace of a second acid.

This colouring matter differed from quercetin, with which it otherwise seemed to be identical, in the fact that dilute alkaline liquids dissolved it with a green coloration. Experiments were therefore undertaken to determine if the reaction was characteristic of the substance or due to impurity.

The green colour was fugitive in character, and as it was possible that the second substance, by which it was presumably caused, might be more readily oxidised in this manner than the colouring matter, the alkaline solution was exposed in a shallow dish to the air, but the green colour did not disappear until the entire substance was decomposed.

The colouring matter was therefore converted into its monopotassium salt (Trans., 1899, 75, 438) and into its sulphate (Trans., 1895, 67, 644), for these operations usually effect a removal of non-tinctorial impurities. The colouring matter regenerated from both compounds, however, still dissolved in alkaline solutions with a green coloration.

With a similar object, but also without success, some quantity of the substance was acetylated, and the product, after repeated crystallisation, decomposed in the usual manner.

2.7767 gave  $1.6410 \text{ C}_{15}\text{H}_{10}\text{O}_7$ .  $\text{C}_{15}\text{H}_{10}\text{O}_7 = 59.09$ .

$\text{C}_{15}\text{H}_8\text{O}_7(\text{O}_2\text{H}_3\text{O})_5$  requires  $\text{C}_{15}\text{H}_{10}\text{O}_7 = 58.98$  per cent.

These results pointed to the fact that the main bulk of the dye-stuff was quercetin, and as its abnormal behaviour with dilute alkali could be explained by the presence of a small quantity of myricetin, which is known to occur in numerous natural tannins, the action of bromine on the colouring matter was studied, the bromo-derivative of quercetin being distinguished from that obtained from myricetin by its sparing solubility in alcohol (Trans., 1896, 69, 1293). The substance made into a thin cream with acetic acid was treated with a slight excess of bromine and left for 48 hours. The greater part of the product crystallised in glistening needles melting at  $243^\circ$  (found  $\text{C} = 40.19$ ;  $\text{H} = 2.96$ ;  $\text{C}_{15}\text{H}_8\text{O}_7\text{Br}_2$  requires  $\text{C} = 39.13$ ;  $\text{H} = 1.74$  per cent.), and appeared to be dibromoquercetin, from which a trace of bromine had been eliminated during the purification. Dibromoquercetin, as Herzig has shown (*Monatsh.*, 1897, 18, 700) is reconverted into quercetin by means of hydriodic acid, and the above product by this method gave a colouring matter which now dissolved in alkalis with a pure yellow colour, and had all the properties of pure quercetin (found  $\text{C} = 59.27$ ;  $\text{H} = 3.88$  per cent.).

The colouring matters of the leaves of *Arctostaphylos Uva ursi* are therefore ellagic acid and quercetin, together with a trace of a dye-stuff soluble in dilute alkalis with a green coloration. The latter is probably myricetin, but this could not be definitely ascertained, owing to the small amount of raw material which the leaves contain.

Broach leaves (Trans., 1897, 73, 384), a South African tannin matter, have been shown to contain a colouring matter,  $\text{C}_{15}\text{H}_{10}\text{O}_7$ , differing only from quercetin by the green colour of its alkaline solutions. There can be little doubt from the above results that this also

is due to the presence of a second colouring matter, which is analogous to, or identical with, myricetin.

*The Leaves of Hæmatoxylon Campeachianum.*

For a supply of the leaves of this plant, I am much indebted to Mr. W. Fawcett, Director of Public Gardens and Plantations, Kingston, Jamaica. They were examined for the presence of a colouring matter, in case this should be chemically related to the hæmatoxylin, which is present in the stem. The isolation of a yellow dye-stuff rendered such a relationship unlikely, but the work was continued in order to study a tannin which was present in some quantity. The dye-stuff was obtained as yellow needles soluble in dilute alkalis with a green coloration.

0.1164 gave 0.2540  $\text{CO}_2$  and 0.0392  $\text{H}_2\text{O}$ .  $\text{C} = 59.51$ ;  $\text{H} = 3.74$ .

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires  $\text{C} = 59.60$ ;  $\text{H} = 3.31$  per cent.

The *acetyl* derivative,  $\text{C}_{15}\text{H}_8\text{O}_7(\text{C}_2\text{H}_5\text{O})_5$ , melted at  $190^\circ$ .

0.1056 gave 0.2258 and 0.0410  $\text{H}_2\text{O}$ .  $\text{C} = 58.31$ ;  $\text{H} = 4.31$ .

$\text{C}_{25}\text{H}_{20}\text{O}_{12}$  requires  $\text{C} = 58.59$ ;  $\text{H} = 3.90$  per cent.

The main products of the action of fused alkali on the colouring matter were *phloroglucinol* and *protocatechuic acid*. The substance therefore appeared to be quercetin, accompanied, like that contained in the bearberry leaves, by myricetin in small quantity. On treatment with bromine, the bulk of the product crystallised from alcohol in yellow needles melting at  $232\text{--}234^\circ$ , and the colouring matter regenerated from this by means of hydriodic acid dissolved in alkalis with a yellow colour, and had the reactions of pure *quercetin*.

*The Tannin.*—The leaves were extracted with boiling alcohol, the extract evaporated to a small bulk, poured into water, and the mixture treated with ether in order to remove wax and chlorophyll. From the brown aqueous liquid, after saturation with salt, the tannin was extracted with ethyl acetate, and the solution cautiously evaporated. The viscous residue was dissolved in water, and salt added, causing the precipitation of a brown impurity, which was removed by agitation with bibulous paper and filtration. By subsequent extraction with ethyl acetate, the tannin was obtained as a yellow, friable mass.

0.1182 gave 0.2304  $\text{CO}_2$  and 0.0428  $\text{H}_2\text{O}$ .  $\text{C} = 53.15$ ;  $\text{H} = 4.02$  per cent.

Digested with boiling dilute sulphuric acid, it yielded *gallic acid*, obtained as needles melting at  $238\text{--}240^\circ$ . As it further gave a bluish-green coloration with aqueous ferric chloride, but no precipitate with boric acid, it was identified as *gallotannic acid*.

Professor H. E. Procter was good enough to undertake an examination of the tanning properties of the leaves, and I am indebted to him for the following account of his results :

Tanning matters .....	9.5 per cent.
Soluble non-tanning matters .....	17.5   ,,
Insoluble at 60° F. ....	62.8   ,,
Water .....	10.2   ,,

100.0

"The tanning strength, 9.5 per cent., is too low to allow of the profitable exportation of the leaves as such, but the colour of the leather tanned by them is by no means bad, and if a satisfactory extract of not less than 25 per cent. strength can be produced from them, it would no doubt find a market in this country."

According to Mr. W. Fawcett, the sample of leaves employed in this investigation was of somewhat poor quality, owing to collection late in the season. It is probable that at an earlier period they contain more tannin, for an analysis of selected leaves gave 11.2 per cent. of tanning matter.

#### *Rhus Metopium.*

I am also indebted to Mr. W. Fawcett for samples of the stems and leaves of this plant. Its comparison with *R. Cotinus* and *R. rhodanthema* was of interest, because the leaves of the latter contain a colouring matter which is distinct from that of the stem (Trans., 1897, 71, 1016). Beyond a trace of ellagic acid, the stem of *R. Metopium* is devoid of colouring matter, and from an examination of other members of this class, the properties of *R. Cotinus* and *R. rhodanthema* in this respect appear to be somewhat exceptional.

The colouring matter of the leaves was obtained in the form of yellow needles soluble in alkaline solutions with a deep green coloration, and seemed to be myricetin, but further experiment revealed the presence of two substances. Thus the acetyl compound had no definite melting point, and, on analysis, gave numbers (C=57.25; H=4.51 per cent.) intermediate between those required by acetylmyricetin and acetylquercetin. To separate as far as possible the constituents of the mixture, this acetyl compound was fractionally crystallised from alcohol, and in this way a less soluble portion was eventually obtained which had the properties of *acetylmyricetin*,  $C_{15}H_4O_8(C_2H_5O)_6$ , and melted at 204–206°.

0.1055 gave 0.2200  $CO_2$  and 0.0396  $H_2O$ . C=56.87; H=4.17.

$C_{27}H_{22}O_{14}$  requires C=56.84; H=3.86 per cent.

A portion was hydrolysed with acid, and the regenerated colouring matter analysed :

0.0953 gave 0.1993  $\text{CO}_2$  and 0.0305  $\text{H}_2\text{O}$ .  $\text{C}=57.03$ ;  $\text{H}=3.54$ .

$\text{C}_{15}\text{H}_{10}\text{O}_8$  requires  $\text{C}=56.60$ ;  $\text{H}=3.14$  per cent.

It was obtained as glistening, yellow needles, and had the characteristic reactions of *myricetin*. The amount present in the leaves is approximately 0.1 per cent.

The identification with certainty of the second colouring matter was more difficult, for it was by far the minor constituent of the mixture. From the more soluble portion of the mixed acetyl derivatives, a fraction was obtained melting at  $189-191^\circ$ , which appeared to be acetyl-quercetin, but the colouring matter regenerated by hydrolysis with acid proved to contain a trace of myricetin. It was therefore treated with bromine, and a compound was thus obtained which melted at  $237-239^\circ$ , and was evidently dibromoquercetin. *Quercetin* is therefore the second colouring matter of the leaves of *R. Metopium*, and its identity was further confirmed by the presence of *protocatechuic acid* among the products formed by the action of fused alkali on the mixed colouring matters. On account of their small quantity, the above products could not be analysed.

In their colouring matters, the leaves of the *Rhus Metopium* resemble those of *R. Cotinus*, *R. rhodanthema*, and *R. Coriaria* previously examined, which contain respectively myricetin, quercetin, and myricetin.

According to the late Professor Henry Trimble, the leaves of *R. metopium* contain gallotannic acid. An analysis gave the following result :

Tanning matters .....	8.2 per cent.
Soluble non-tanning matters.....	13.0 "
Insoluble at $60^\circ \text{F}$ . ....	68.5 "
Water .....	10.3 "
	<hr/>
	100.0

#### *Coriaria myrtifolia*.

*Coriaria myrtifolia* is a low, deciduous shrub, native of Southern Europe, and is employed in dyeing black. It has been examined by Riban (*Zeit. Chem.*, 1867, 663), who isolated from it the poisonous glucoside, coriamyrtin. For a supply of the leaves, I am much indebted to the kindness of Professor Maxime Cornu, of the Museum d'Histoire Naturelle, at Paris. The crude yellow colouring matter, isolated in the usual manner, contained ellagic acid, which, on extraction with alcohol, remained undissolved, and was identified by the usual tests.



The alcoholic extract was evaporated to a small bulk and diluted with boiling water, and the colouring matter which thus separated was collected and crystallised from dilute alcohol. It formed glistening, yellow needles soluble in alkaline solutions with a yellow colour.

0.1126 gave 0.2456  $\text{CO}_2$  and 0.0350  $\text{H}_2\text{O}$ .  $\text{C}=59.48$ ;  $\text{H}=3.45$ .

$\text{C}_{15}\text{H}_{10}\text{O}_7$  requires  $\text{C}=59.60$ ;  $\text{H}=3.31$  per cent.

The acetyl compound,  $\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$ , was obtained as colourless needles melting at  $191^\circ$ .

0.1135 gave 0.2421  $\text{CO}_2$  and 0.0450  $\text{H}_2\text{O}$ .  $\text{C}=58.17$ ;  $\text{H}=4.40$ .

$\text{C}_{25}\text{H}_{20}\text{O}_{12}$  requires  $\text{C}=58.59$ ;  $\text{H}=3.90$  per cent.

As fusion with alkali gave *phloroglucinol* and *protocatechuic acid*, this colouring matter was evidently *quercetin*.

The tannin of this plant is known to be gallotannic acid, and evidence of this was forthcoming by the isolation of much gallic acid during the extraction of the colouring matter. An analysis, carried out under the direction of Professor Procter, gave the following result :

Tanning matter.....	15.6 per cent.
Soluble non-tanning matters.....	27.4 "
Insoluble at $60^\circ$ F. ....	43.7 "
Water.....	13.3 "

100.0

The colour of leather tanned by these leaves is very satisfactory, and practically equal to that produced by genuine sumach (*R. Coriaria*); the strength in tanning matter, however, is considerably inferior, good samples of sumach reaching 25 and even 30 per cent. of this material.

### *Myrica Gale.*

Though it has been shown that myricetin exists in numerous plants, with the exception of the *Myrica Nagi*, which is difficult to obtain, the quantity present in each is so very small that its further examination has been of necessity postponed until a more fruitful source is discovered. With the latter object *M. Gale*, the ordinary bog-myrtle, was examined, in the hope that it might contain some quantity of the colouring matter. For a supply of the bark and leaves, I am indebted to the kindness of Professor J. J. Hummel.

The colouring matter of the leaves was obtained as glistening, yellow needles, soluble in alkalis with a green coloration. The yield was approximately 0.1 per cent.

Found  $\text{C}=56.57$ ;  $\text{H}=3.69$ .

$\text{C}_{15}\text{H}_{10}\text{O}_8$  requires  $\text{C}=56.60$ ;  $\text{H}=3.14$  per cent.

The acetyl compound,  $C_{15}H_4O_8(C_2H_3O)_6$ , formed colourless needles melting at  $204-206^\circ$ .

Found C = 56.57 ; H = 3.86.

$C_{27}H_{22}O_{14}$  requires C = 56.84 ; H = 3.86 per cent.

On fusion with alkali, *phloroglucinol* and an acid resembling *gallic* acid were obtained ; the colouring matter was therefore *myricetin*, but although the result is interesting, in that it confirms the conclusions of the botanist, *M. Gale* cannot be employed as a source of this colouring matter in quantity. The bark was almost devoid of dyeing properties, but appeared to contain a gallotannin.

The experiments on this plant were largely carried out by Mr. I. E. J. Wilkinson, to whom my best thanks are due.

#### *The Leaves of Robinia pseudacacia.*

The *Robinia pseudacacia* (common or false acacia, North American locust) is a native of the United States, from Pennsylvania southward to Carolina, where its timber is extensively employed. It is also cultivated in France. The flowers have been examined by Zwenger and Dronke (*Annalen, Suppl.*, 1861, 1, 257), who isolated from them a quercetin glucoside, robinin, which differed from quercitrin in yielding no precipitate with lead acetate. For a liberal supply of the bark, stem, and leaves, I am much indebted to Dr. M. Jarry of Paris.

A boiling aqueous decoction of the leaves was treated with basic lead acetate solution, and the resulting pale yellow precipitate suspended in water and decomposed with boiling dilute sulphuric acid. From the clear liquid decanted from the lead sulphate, the colouring matter was removed by extraction with ether and purified by crystallisation from dilute alcohol. The yield was 0.14 per cent. of the crude substance, and this, on purification, was reduced approximately by one-half.

0.0969 gave 0.2412  $CO_2$  and 0.0442  $H_2O$ . C = 67.83 ; H = 5.06.

0.1126 „ 0.2787  $CO_2$  „ 0.0490  $H_2O$ . C = 67.49 ; H = 4.84.

$C_{16}H_{12}O_5$  requires C = 67.60 ; H = 4.22 per cent.

This new colouring matter, for which the name *acacetin* is proposed, forms almost colourless needles, soluble in alkalis with a pale yellow coloration. With alcoholic lead acetate, it yields a yellow precipitate, but owing to the instability of this compound in the presence of dilute acetic acid, it is not entirely precipitated in this manner. It does not yield a salt with potassium acetate, or compounds with mineral acids, and the inference that it does not contain hydroxyl groups in relatively ortho-positions is also borne out by its feeble dyeing properties. With

sulphuric acid, it gives a pale yellow solution, and with alcoholic ferric chloride a deep reddish-brown coloration.

The *acetyl* derivative,  $C_{16}H_{10}O_5(C_2H_3O)_2$ , formed colourless needles melting at 195—198°, and is sparingly soluble in alcohol.

0.1002 gave 0.2373  $CO_2$  and 0.0390  $H_2O$ .  $C = 64.58$ ;  $H = 4.32$ .

$C_{20}H_{16}O_7$  requires  $C = 65.21$ ;  $H = 4.35$  per cent.

By decomposition with fused alkali, acacetin yielded *phloroglucinol*, and an acid melting at 210° having the reactions of *p-hydroxybenzoic acid*. In the crude condition, the latter was contaminated with a trace of a second acid, which gave with aqueous ferric chloride a green coloration, and appeared to be protocatechuic acid. The colouring matter contained one methoxy-group.

0.1414 gave 0.1085 AgI.  $CH_3 = 4.89$ .

$C_{15}H_9O_4(O \cdot CH_3)$  requires  $CH_3 = 5.28$  per cent.

The hydriodic acid left in the distilling flask in this determination was poured into a solution of sodium hydrogen sulphite, and the precipitate collected and purified by crystallisation from dilute alcohol.

0.1075 gave 0.2615  $CO_2$  and 0.0390  $H_2O$ .  $C = 66.34$ ;  $H = 4.03$ .

$C_{15}H_{10}O_5$  requires  $C = 66.66$ ;  $H = 3.70$  per cent.

The product was obtained as almost colourless needles, soluble in alkalis with a pale yellow coloration. With alcoholic ferric chloride, a deep reddish-brown liquid was obtained, and these reactions, together with its dyeing properties, indicated its identity with *apigenin*, the colouring matter of parsley (Trans., 1897, 71, 805). This conclusion is in harmony with all the results of the investigation, and there can be little doubt that acacetin is a *monomethyl ether of apigenin*. The amount of acacetin available for this work was only 2 grams, consequently a further characterisation of the apigenin was impossible. When a new supply of raw material can be obtained, this colouring matter will be further studied.

It is interesting to note that whereas an apigenin monomethyl ether, as a glucoside, is contained in the leaves of this plant, a quercetin glucoside occurs in the flowers (Zwenger and Dronke, *loc. cit.*), quercetin being probably a dihydroxyapigenin. If opportunity occurs, a re-investigation of robinin will be undertaken.

The stem and bark of *Robinia pseudacacia* are devoid of colouring matter.

*Tanning Properties.*—The following analyses of the leaves and the bark were carried out under the direction of Professor Procter:

	Leaves.	Bark.
Tanning matters .....	8.2	2.8 per cent.
Soluble non-tanning matters ...	9.5	12.8 „
Insoluble in water at 60° F.....	73.4	75.3 „
Water .....	8.9	9.1 „
	<hr/> 100.0	<hr/> 100.0

The leaves contain too small an amount of tannin to be of much value as a tanning material, and the bark is practically worthless in this respect. Qualitative tests indicated the absence of tannin in the stem of the plant.

The author is indebted to the Research Fund Committee of the Chemical Society for a grant which has been in part employed for expenses of this investigation.

CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
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### XLIII.—*Potassium Nitrito-hydroximidosulphates and the Non-existence of Dihydroxylamine Derivatives.*

By EDWARD DIVERS, M.D., D.Sc., F.R.S., Emeritus Professor of Chemistry, and TAMEMASA HAGA, D.Sc., Professor of Chemistry in the Tōkyō Imperial University, Japan.

LIKE potassium nitrate (Trans., 1894, 65, 523), potassium nitrite forms double salts with the potassium hydroximidosulphates (sulphonates); and the non-recognition of their existence has given rise to mistaken notions as to the nature of the products produced by the sulphonation of nitrous acid.

*Potassium Nitrite and 2/3 Normal Hydroximidosulphate,*  
 $\text{KNO}_2, \text{HON}(\text{SO}_3\text{K})_2$ .

—The sparing solubility of 2/3 normal potassium hydroximidosulphate in water is so little affected by the presence of potassium nitrite, that it crystallises out again almost pure on cooling a hot solution, even if this contains as much as one-sixth of its weight of the nitrite; when however, more nitrite than this is present, a salt separates which is a compound of the hydroximidosulphate with a mol. of the nitrite, and the same double salt is formed in the cold when the hydroximidosulphate is triturated with a strong solution of the nitrite in excess. If precautions are taken against the hydrolysis of the

very unstable hydroximidosulphate, this salt can be dissolved at  $70^{\circ}$  in as little as 3.8 times its weight of a 22 per cent. solution of nitrite, and on cooling, the solution deposits the crystalline double salt in quantity equivalent to about 12/13 of the hydroximidosulphate.

Whilst the hydroximidosulphate itself crystallises in hard, rhombic prisms with  $2\text{H}_2\text{O}$ , its compound with the nitrite forms silky, asbestos-like fibres, which are anhydrous; the compound salt differs also from potassium nitrite in not being deliquescent, but in other properties, is indistinguishable from a mixture of its component salts. It can be recrystallised from a hot 10 per cent. solution of potassium nitrite. It is neutral to litmus and very soluble in water, but its solution soon deposits crystals of the 2/3 normal potassium hydroximidosulphate, unless it is very dilute. In any case, the hydroximidosulphate can be separated from the nitrite by precipitating it with barium hydroxide. Like a hydroximidosulphate (*Trans., loc. cit.*), the solid salt, when digested with a highly concentrated solution of potassium hydroxide, is converted into sulphite and nitrite. When acidified, its solution becomes yellowish, and soon effervesces from escape of nitrous oxide, leaving potassium hydrogen sulphate in solution; this effect is due to the hydroximidosulphate being a sulphonated hydroxylamine, and hydroxylamine, with nitrous acid, decomposing into nitrous oxide and water. It decomposes explosively when heated—more so than does the hydroximidosulphate by itself—giving off almost colourless gases and white fumes.

The compound salt can be purified from other salts or from alkali by recrystallisation from a sufficiently concentrated potassium nitrite solution, but from its own mother-liquor it must be separated by draining on a tile, such draining being very effective because of the felted, fibrous form of the salt, its non-deliquescent nature, and the hygroscopic character of a solution of potassium nitrite. The analysis of the salt was made in the usual way described in our previous papers on hydroximidosulphates and other sulphonated nitrite derivatives. By boiling its solution with an acid, most of its sulphur appears as ordinary sulphate, but not quite all; so that, in estimating the sulphur, the solution must be hydrolysed for some hours at  $150^{\circ}$  under pressure.

	Potassium.	Sulphur.
Found .....	33.14	17.95 per cent.
$\text{K}_3\text{HN}_2\text{S}_2\text{O}_5$ requires .....	33.10	18.06 ,,

There are other ways in which the potassium nitrito-2/3 normal hydroximidosulphate may be formed, all consisting essentially in producing the hydroximidosulphate by sulphonating a small portion of the potassium nitrite in a concentrated solution. Thus, the following mode

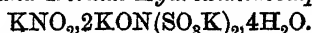
of working will give good results with certainty, but it may be widely deviated from with due consideration and precaution, provided only that a concentrated solution of nitrite be employed. Potassium nitrite, 30 grams; potassium hydroxide, 10 grams; water, 50 to 100 grams, are to receive a current of sulphur dioxide freely until crystals begin to form, the containing flask being all the time agitated in a cooling bath of ice and brine. The sulphur dioxide is now passed in more slowly for some time longer, and then stopped. After half an hour, the salt deposited from the solution is collected and drained on a tile. Its mother liquor is alkaline to litmus, but not to rosolic acid (presence of sulphite, absence of alkali); the well-drained salt itself is only faintly, if at all, alkaline to litmus. The double salt is also produced when to an ice-cold, nearly saturated solution of potassium nitrite, a similar solution of potassium pyrosulphite is very slowly added until crystallisation begins, and the solution is allowed to stand for some time. Prepared in this way, the compound salt is liable to be contaminated with a little nitrilosulphate and sulphite. The experiment just described was made first by Raschig, but he attached to it a significance unlike that here presented. Discussion of his views will be found towards the end of this paper.

There is yet another way in which this potassium nitrito-hydroximidosulphate can be produced, which it is of interest to mention, because it illustrates the decomposibility of potassium  $\frac{5}{6}$  normal hydroximidosulphate into the normal and  $\frac{2}{3}$  normal salts. While the  $\frac{2}{3}$  normal salt dissolved in 16 per cent. or stronger solutions of the nitrite, crystallises out only in combination with nitrite, the  $\frac{5}{6}$  normal salt, when dissolved in a nitrite solution of even 50 per cent., for the most part crystallises out again uncombined; generally, however, with this strength of nitrite solution, a little fluffy or cotton-like, lustreless matter also separates. If now, to this fluffy matter, suspended in its cold mother liquor carefully decanted from every particle of the crystals of the  $\frac{5}{6}$  normal salt, a hot solution of this  $\frac{5}{6}$  normal salt in 50 or even 40 per cent. nitrite be poured in, a relatively large quantity of the fluffy matter is obtained, and not the hard prisms of the  $\frac{5}{6}$  normal salt. Under the microscope, the fluffy matter proves to be crystalline, and when drained on a tile it has a silvery lustre; on analysis, it is found to be the nitrito- $\frac{2}{3}$  normal hydroximidosulphate, only slightly impure from the presence of a little  $\frac{5}{6}$  normal hydroximidosulphate and nitrite. Thus, in place of potassium 33.10, and sulphur 18.06, per cent., we found in it 33.79 and 18.35 respectively, together with an alkalinity equal to 1.09 per cent. potassium. If dissolved in hot 12 per cent. nitrite solution, it recrystallises as the pure double salt. It is thus apparent that in a very concentrated solution of nitrite containing the  $\frac{5}{6}$  normal salt

dissolved in it, there is unstable equilibrium between the tendency to yield  $\text{HON}(\text{SO}_3\text{K})_2, \text{KON}(\text{SO}_3\text{K})_2, \text{H}_2\text{O}$  again, and that to form  $\text{HON}(\text{SO}_3\text{K})_2, \text{KONO}$ .

Sodium nitrite forms a compound with sodium 2/3 normal hydroximidosulphate, which has not been further examined, principally because of its great solubility in sodium nitrite solution.

*Potassium Nitrite and Normal Hydroximidosulphate,*



—This compound salt is only obtainable from a strongly alkaline solution, for when the normal hydroximidosulphate is dissolved in a hot concentrated solution of the nitrite, only the 5/6 normal hydroximidosulphate crystallises out on cooling, just as it would do in the absence of nitrite. In order to crystallise out either the normal hydroximidosulphate (*Trans.*, *loc. cit.*) or its combination with nitrite, free alkali must be present in some quantity. When, however, too much alkali is present, a little of it deposits with the normal salt or with the nitrito-normal salt (in place apparently of water of crystallisation, *Trans.*, *loc. cit.*), and then lessens the capacity of the normal salt to combine with nitrite. The double salt is readily obtained by dissolving normal hydroximidosulphate nearly to saturation in a hot ( $70^\circ$ ) solution consisting of 33—66 parts nitrite and 3—5 parts hydroxide to 100 parts water, and cooling. Usually, it forms lustrous, silky fibres, like those of the 2/3 normal double salt, but radiating from points to form voluminous, soft, spherical masses. When the solution is more strongly alkaline, the double salt separates as nearly opaque, spherical granules, sometimes with long fibres growing out from them. Under the microscope, these granules are seen to have also a radiating fibrous structure, and to represent the soft, voluminous spheres highly condensed; probably the latter always begin their growth from a minute granular nucleus. The double salt can only be purified for analysis by pressing it on the porous tile, when the soft spheres become a felted, lustrous cake, and the hard, white granules crumble down like masses of wax.

	Potassium.	Sulphur.	Alk. potassium.
Silky, found ... ..	35.21	16.23	9.92 per cent.
$\text{K}_7\text{N}_3\text{S}_4\text{O}_{16}, 4.4\text{H}_2\text{O}$ .....	35.14	16.43	10.04 „
Granular, found .....	33.99	15.90	9.20 „
$\text{K}_7\text{N}_3\text{S}_4\text{O}_{16}, 6\text{H}_2\text{O}$ .....	33.89	15.85	9.68 „

The varying amount of water is only the recurrence of what we have recorded in the case of normal potassium hydroximidosulphate. The double salt is exceedingly alkaline; its alkalinity we estimated by means of decinormal acid and litmus.

Like the previously described double salt, it is but little soluble in

concentrated nitrite solution, although freely soluble in water, which decomposes it into its constituent salts, and also decomposes one of these, the normal hydroximidodisulphate, into alkali and crystals of the 5/6 normal salt. When heated, it decomposes suddenly, but gently, without fusing or scattering, and evolves slight red fumes but no white ones. By this behaviour, it was easily distinguishable from the 2/3 normal double salt, and also from any other hydroximidodisulphate which, simple or combined with nitrite, contained less than its  $K_7$  to  $S_4$ . By dissolving the nitrito-2/3 normal hydroximidodisulphate in a hot concentrated solution of nitrite containing sufficient alkali, the nitrito-normal hydroximidodisulphate can be readily obtained on cooling the solution.

*Potassium Nitrite and 5/6 Normal Hydroximidodisulphate.*—We have obtained three compounds of the 5/6 normal salt with nitrite, one being  $7KNO_2 \cdot 2K_5H(NS_2O_7)_2 \cdot 3H_2O$ . By using an almost saturated solution of potassium nitrite containing a little potassium hydroxide, and dissolving in it, by heat, the 5/6 normal hydroximidodisulphate, a compound is obtained in minute, fibrous crystals, very lustrous when dry; this is decomposed by water, but may be recrystallised from a saturated nitrite solution. The same salt can be obtained also by dissolving the nitrito-normal hydroximidodisulphate in a hot, almost saturated solution of nitrite.

When heated, it is feebly explosive. Its composition approaches that indicated by the formula given above. For analysis, it was only air-dried on a tile; in the desiccator, it would probably have lost its 3 per cent. of water ( $= 3H_2O$ ), and then approached in composition Fremy's *sulphazite* :

	Potassium.	Sulphur.	Alk. potassium.
Original salt, found.....	36.81	14.35	4.80 per cent.
Recrystallised .....	36.68	14.47	4.51 „
$K_{17}H_3N_{11}S_8O_{42} \cdot 3H_2O$ ...	36.87	14.20	4.34 „

A second double salt,  $3KNO_2 \cdot K_5H(NS_2O_7)_2 \cdot H_2O$ , was prepared by dissolving 1 mol. of 5/6 normal salt and 1.4 mols. of potassium hydroxide in a hot 65 per cent. nitrite solution, and cooling. In appearance, it resembled the other compound salt.

	Potassium.	Sulphur.	Alk. potassium.
Found.....	36.17	15.07	4.51 per cent.
Calculated .....	36.81	15.06	4.60 „

A third double salt, anhydrous,  $7KNO_2 \cdot 3K_5H(NS_2O_7)_2$ , was not prepared synthetically, but was obtained by treating an almost saturated solution of the nitrite with alkali and sulphur dioxide, and adding alkali again after the sulphonation, imitating a process of Fremy's. On filtering the heated solution from much crystalline 5/6 normal hydroximidodisulphate,



sulphate mixed with a little of its combination with nitrite, and allowing the mother liquor to cool, it became almost filled with tiny prisms of a compound answering to the above formula :

	Potassium.	Sulphur.	Alk. potassium.
Found .....	36.94	16.37	4.96 per cent.
Calculated .....	36.99	16.51	5.05 „

This salt was quickly resolved by water into nitrite and crystals of the very sparingly soluble 5/6 normal hydroximidosulphate.

The varying proportions in which potassium nitrite and the 5/6 normal hydroximidosulphate unite would possess but little interest, were it not for the fact that they have evidently been severally met with and taken to be salts of specific constitution by Fremy and by Raschig.

*Non-existence of Dihydroxylaminesulphonates.*

Fremy believed in the existence of less sulphonated derivatives of potassium nitrite than his *sulphazite* (see next paper), itself less sulphonated than his *sulphazotates* (hydroximidosulphates), and attributed his failure to find them to the fact of their excessive solubility. Claus held much the same views, and believed that by adding to an aqueous solution of potassium nitrite an alcoholic solution of sulphur dioxide in not too large a quantity, he had obtained an impure crystallisation of a salt,  $\text{ON} \cdot \text{SO}_3\text{K}$  (*Ber.*, 1870, 4, 508). He did not prove this to be the case, but what he did publish about his product is sufficient to show that it was the compound of potassium nitrite with 2/3 normal hydroximidosulphate we have described in this paper. A repetition of his experiment gave us this double salt, together with much ethyl nitrite. Raschig regarded Claus's preparation as essentially the same as one of his own salts, to which he gave the constitution of basic dihydroxylaminesulphonate derivatives with the following formulæ :



These he prepared by partial sulphonation of the nitrite in known ways. They both yielded crystals of a hydroximidosulphate when dissolved in a little water, and differed in no essential particular from nitrito-hydroximidosulphates. We found that hot solutions of nitrite and a hydroximidosulphate, on cooling, deposited an apparently homogeneous crop of crystals of almost the same composition and properties as one or other of Raschig's salts. Raschig gave two ways for preparing the salt having the second of the formulæ just given, and in these ways we have obtained the nitrito-2/3 normal hydroximidosulphate already described in this paper, but mixed with a little potassium

sulphite. This impurity accounts for the alkaline reaction of Raschig's preparation and the presence in it of a little more than  $K_8$  to  $S_2$ .

He obtained the other salt ( $K_2$  to  $S$ ) only once, and in the form of white crusts, when working unsuccessfully for hydroximidosulphate in Claus's way, the other main product being imidosulphate, that is, hydrolysed nitrilosulphate, as he himself pointed out. Following Fremy's method, we have obtained—also by sulphonating nitrite—a product qualitatively like Raschig's salt, although differing a little from it quantitatively, and, at the same time, like the second salt compounded of nitrite and  $5/6$  normal hydroximidosulphate described by us on page 436. The percentages found by Raschig were potassium, 36.84, and sulphur 15.50.

When Raschig's salt was dissolved in water and acidified, it gave nitrous oxide as the only gaseous product, whilst ours gave also some nitric oxide. This fact might have served to render incorrect the application of our formula to his salt, but for the evidence there is that it was mixed with a little sulphite, which would have reduced any nitric oxide. Its mother liquor, on further evaporation, gave, we are told, so much sulphite along with the next crop of the salt itself, as to cause its rejection. The presence of sulphite in less quantity in the first crop of crystals will have been masked by the oxidising action of the nitric oxide in becoming nitrous oxide. That sulphite was present in Raschig's preparation well accords also with the fact that potassium hydroxide added in excess precipitated potassium sulphite, for, although hydroximidosulphate is itself decomposed by the most concentrated solutions of potassium hydroxide into sulphite and nitrite, this decomposition is slow, and the sulphite is deposited only after some time. Raschig's preparation, when dried on a tile, was only a powder—that is, presumably, was not obviously crystalline—a point which also indicates an impure salt. Since the potassium and sulphur are in the same ratio in the two salts, quantitative analysis would hardly have made its presence known.\* Inspection of Raschig's formulæ is of itself sufficient to prevent their being accepted as in accordance with the facts; for, from these formulæ, both salts should be strongly alkaline, whilst, in reality, one is neutral. Above all, it is hardly credible that dissolution in cold water should suffice to cause monosulphonated nitrogen to become disulphonated.

Raschig held his two salts to be identical with Fremy's *potassium sulphazite* and *sulphazate* respectively; but the nature of Fremy's salts

\* Of the  $3KNO_2$  of our formula, only 1 mol. can give nitric oxide and that only to the extent of two-thirds of its nitrogen, the other third becoming nitric acid. Raschig's analysis indicates the presence of only  $3/4$  mol. active nitrite. The quantity of hydrated sulphite required to be present is therefore only 5.2 per cent. of the mixed salts.

will be found, we believe, more precisely given in the paper following this. The point we would here insist on is that Raschig's preparations, judged by their chemical behaviour, have no claim to be considered as *dihydroxylamine* derivatives, being in every way indistinguishable from synthetically prepared compounds of nitrite and hydroximidosulphates. Dihydroxylamine salts have as yet only a hypothetical existence, and are likely to remain so, for the double linking of the oxygen atom with the tervalent or quinquivalent nitrogen atom seems always experimentally to make or break itself in a single act, notwithstanding its bipartite character.

Raschig, in his researches on Fremy's sulphazotised salts, obtained, besides those we have just discussed, two other salts of undetermined constitution, both of which were most probably also nitrito-hydroximidosulphates. They may therefore be noticed here, although Raschig did not represent them to be dihydroxylamine derivatives. Yet they evidently closely resembled the other two in properties. One was isomeric with potassium hyponitrososulphate (Pelouze's salt), and also with his ( $K_2$  to S) dihydroxylamine salt, allowing for difference in hydration, and the other was isomeric with potassium  $5/6$  normal hydroximidosulphate. Each could be obtained but once, and they only call for any detailed notice because of the theoretical importance given to them as isomerides of other salts. The first referred to above was mistaken by Raschig for Pelouze's salt (hyponitrososulphate), but that salt it certainly was not (Trans., 1895, 67, 453). It was prepared by dissolving nitric oxide in solution of potassium sulphite and hydroxide, and evaporating to a small volume until crusts formed. If we assume that air or nitric peroxide was not excluded, the conditions were present for getting a nitrito-hydroximidosulphate, for, as we hope to show in a paper which will shortly follow this, nitrous fumes passed into potassium sulphite solution generate hydroximidosulphate freely, together with nitrite.

The other salt, isomeric with  $5/6$  normal hydroximidosulphate, was obtained in Raschig's attempt to form the  $2/3$  normal salt by passing sulphur dioxide into a solution of potassium nitrite and hydroxide and leaving the mixture for a day. These, too, are conditions for the formation of nitrito-hydroximidosulphate. Now both products were decomposed by water in such a way as to yield hydroximidosulphate, whilst in other ways they behaved as compounds of nitrite with one of these salts. The behaviour of the product isomeric with hyponitrososulphate was indeed exceptional, in that, when dissolved in water containing a little alkali, it gave the  $2/3$  normal hydroximidosulphate, although, according to our calculation, it should have given the  $5/6$  normal salt; moreover, it also gave, in hot alkaline

solution, a little nitrous oxide, which only hydroxyamidodisulphate is known to give. These peculiarities we may attribute to partial hydrolysis having occurred in the very unstable salt before these experiments were made.

The calculated formula for the isomeride of hyponitrosodisulphate as a nitrite compound is  $3\text{KNO}_2, \text{K}_5\text{H}(\text{NS}_2\text{O}_7)_2, 2\text{H}_2\text{O}$ , and such a compound we have described on page 436; that for the isomeride of the 5/6 normal hydroximidosulphate treated as being a nitrite compound is  $3\text{KNO}_2, 6\text{K}_2\text{HNS}_2\text{O}_7, 5\text{K}_5\text{H}(\text{NS}_2\text{O}_7)_2$ , which in water should give crystals of  $\text{K}_2\text{HNS}_2\text{O}_7, 2\text{H}_2\text{O}$ . This compound salt we have failed to obtain, but its occurrence can be readily accepted as possible. Its assumed existence affords a much more satisfactory explanation of the nature of this salt of Raschig's than that we were able to offer in our paper on hydroximidosulphates already referred to.

	Potassium.	Sulphur.
Nitroso-isomeride, found.....	35.72	14.40 per cent.
Calculated.....	36.05	14.75     „
D. and H.'s salt, found .....	36.17	15.05     „
Oximido-isomeride .....	33.04	21.23     „
Calculated.....	32.91	21.54     „

For the present, the existence of isomerides of Pelouze's salt and Fremy's *basic sulphazotate* must be regarded as no longer even probable.

#### XLIV.—Identification and Constitution of Fremy's Sulphazotised Salts of Potassium.

By EDWARD DIVERS and TANEMASA HAGA.

FREMY found that a sufficiently concentrated solution of potassium nitrite and hydroxide, when treated with sulphur dioxide, gave minute, silky needles of a salt which he provisionally named *potassium sulphazate*. With a slightly diminished concentration of the solution, he generally obtained, instead of this, the brilliant, often hard, rhombic prisms of *potassium basic sulphazotate* (5/6 normal hydroximidosulphate, Trans., 1894, 65, 523). Sometimes, however, neither of these salts was obtained before the solution became transformed into a starch-like jelly through the formation of a salt which he named *potassium metasulphazate*, or else became filled with spangles of yet another salt called by him *potassium metasulphazate*. When the solution was a little too dilute to give any

of these, and if too much alkali had not been added, peculiarly pointed crystals usually appeared consisting of the salt he named *potassium neutral sulphazotate* ( $2/3$  normal hydroximidosulphate, Raschig), and lastly, with still greater dilution, the minute, brilliant needles of the *potassium sulphammonate* (nitrilosulphate, Berglund). He believed also that other salts were produced in the first stages of the reaction, one of which he named *potassium sulphazite*, but this he did not succeed in isolating, assigning as a reason the excessive solubility of the salt. He prepared it—but only in very small quantity and as crystalline, warty granules—by the action of water on the ‘sulphazate,’ whereby this was converted into ‘basic sulphazotate’ which was deposited, and a solution that on evaporation yielded the ‘sulphazite.’ These two salts, if dissolved together, were changed back again into the ‘metasulphazotate,’ whilst the ‘sulphazite’ and the ‘sulphazate’ could similarly often be changed into the ‘metasulphazate’ again. These two meta-salts he regarded, therefore, as perhaps merely double salts of the others. The ‘sulphazite,’ the ‘sulphazate,’ and the ‘sulphazotates’ he treated as being members of a series of salts in which there were two atoms of nitrogen, and from one up to eight atoms of sulphur,—three in the ‘sulphazite,’ four in the ‘sulphazate,’ and five in the ‘sulphazotates.’ With this conception of the nature of these salts, based on his analyses, it was easy to understand the decomposition of the ‘sulphazate’ into the ‘sulphazite’ and the ‘sulphazotate.’ But this and other of Fremy’s interpretations of the facts observed by him have lost all importance and particular interest through the progress of chemistry since his memoir was published.

Subsequent work by others and by us in the same field has shown that Fremy, in the account he gave of the preparation of his many salts, went too little into details as to the conditions under which they were obtained—apparently because he was not able to be more precise. When Claus attempted to prepare Fremy’s salts, he obtained only masses of minute crystals of salts, of whose individuality and nature he could make out but little because of the impossibility of dissolving them entirely without decomposition. In his experiments, the ‘sulphammonate’ (nitrilosulphate) was always formed in considerable quantity, either as a first or secondary product, and by its presence prevented any satisfactory investigation of the other salts. In Fremy’s working, this most easily formed salt came only as the final product of the sulphonation and therefore gave him no trouble. Claus emphatically displayed his scepticism as to Fremy’s results; yet in nearly every point in which he differed from Fremy as to the facts, we find Fremy to have been right. When Raschig repeated Fremy’s work—but with the modifications in procedure introduced by

*Claus*—he obtained results similar to, although less unsatisfactory than, those recorded by Claus, and he made an approach to Fremy's work in so far as that he often got very little nitrilosulphate; nevertheless, he too failed in his attempts to prepare the 'sulphazate' in Fremy's way.

In perhaps all essential points we can lay down the method to repeat Fremy's experimental work successfully. In some cases, however, a little uncertainty obtains owing to the fact that the very concentrated and complex solutions which yield Fremy's salts are apt to deposit what is virtually the same salt in different forms and also, at times, salts quite distinct from each other; there being only slight and obscure variations in the circumstances attending their formation.

*Sulphazate*.—This is Fremy's first salt directly obtained in his sulphonation of the nitrite. In getting it, he took approximately 5 mols. of potassium nitrite to 2 mols. of potassium hydroxide and a little water, and into the solution passed sulphur dioxide until it became almost filled with silky needles very soluble in water. So far, it is easy to follow Fremy with a full measure of success, if only the water used is limited to perhaps twice the weight of the nitrite, and that the heating produced by the action is counteracted by cooling. Claus, and after him Raschig, failed, but then inexplicably to us they did not start with Fremy's proportions of nitrite to hydroxide, although even with the proportions they took, success is possible if care be taken. The salt thus formed by Fremy was not tested and analysed by him until after it had been changed (but without his having recognised the fact) by the further treatment to which he submitted it. Before change, it is the potassium nitrito- $\frac{2}{3}$  normal hydroximidosulphate described in the preceding paper, a neutral salt which is decomposed into its constituent salts by water. Fremy's finished 'sulphazate' was strongly alkaline and very caustic, and when decomposed by water gave nitrite and the  $\frac{5}{6}$  normal hydroximidosulphate—not the  $\frac{2}{3}$  normal salt. Also the analysis he gave of it furnished numbers such as the original product could not have given. Instead of potassium, 33.10, sulphur, 18.06, and nitrogen, 7.9 per cent., he obtained potassium, 34.90, sulphur, 19.55, and nitrogen, 4.9 per cent. We can learn what his after-treatment was by reference to other parts of his paper where he speaks of the care necessary (when sulphonating the nitrite) to maintain the alkalinity of the solution by adding potassium hydroxide from time to time, and of dissolving sulphazotised salts, for examination, in water containing this alkali. It seems certain that he must have added some potassium hydroxide to the solution after getting it to crystallise, as a precaution to preserve the salt; now the effect of this addition is to change the composition of the product without much affecting its silky, asbestos-like appearance. The change it

thus undergoes deprives it of much of its nitrite and converts the  $2/3$  normal into more nearly normal hydroximidosulphate—replacing, therefore, potassium nitrite by potassium hydroxide. Accepting Fremy's mean numbers as accurate, what he analysed had the composition  $11K_3NS_2O_7, H_2O$ ;  $K_2HNS_2O_7, 2H_2O$ ;  $2(K_2HNS_2O_7, KNO_2)$ .

	Potassium.	Sulphur.	Nitrogen.	Alk. potassium.
Found .....	34.9	19.55	4.9	— per cent.
Calculated ...	34.9	19.51	4.9	9.36 ,,

His analyses, however, have no claim to receive such close treatment, his nitrogen seemingly being always much too low; and it is sufficient to say of his 'sulphazate' that it was the silky, asbestos-like, nitrito- $2/3$  normal hydroximidosulphate more or less converted into the also silky, asbestos-like normal hydroximidosulphate, and with this Fremy's description of its other properties entirely agrees. With dilute acids, it slowly evolves nitrous oxide unmixed with nitric oxide. Fremy specially points out that no *sulphazic acid* or any other *sulphazates* could be obtained from the potassium salt. There is, therefore, nothing to justify belief in this compound being the salt of a particular single acid, the *sulphazic*.

*Sulphazite*.—What Fremy named *potassium sulphazite*, he only once obtained (and then not by direct sulphonation of the nitrite) in mammillated, white, crystalline crusts from a solution thickened by the other salts contained in it. That is to say, his *sulphazate* when dissolved in a little water containing some potassium hydroxide, deposited crystals of *basic sulphazotate* ( $5/6$  normal hydroximidosulphate) and left a mother liquor which on evaporation in the cold until it became syrupy yielded the *sulphazite*. It showed great analogy with his *sulphazate*, but was distinguished from it by having little tendency to hydrolyse, and by at once evolving some nitric oxide when its solution was mixed with a dilute acid. Water decomposed the *sulphazite*, but into what products was not ascertained.

We have sufficiently realised Fremy's expectations that his *sulphazite* might directly result from sulphonating the nitrite with subsequent addition of alkali. The substance obtained in this way did not differ greatly in composition from his:

	Potassium.	Sulphur.
Fremy's salt.....	38.16	16.27 per cent.
D. and H.'s salt ...	36.94	16.37 ,,

and agreed with it in chemical properties, so far as is known. At the same time, it was indistinguishable from a compound of nitrite with  $5/6$  normal hydroximidosulphate, the third one described by us as such in the preceding paper (p. 436). Other experiments of various

kinds have yielded us such 'mammillated crusts' as Fremy obtained which, although only in rough agreement in percentage composition with his sulphazite, behaved like it, and proved to be impure double salts of nitrite with  $5/6$  normal or more nearly normal hydroximidosulphate. We are therefore convinced that his sulphazite was merely such a double salt.

*Metasulphazate.\**—In Fremy's experience, when passing sulphur dioxide into the solution of nitrite and alkali of a concentration intermediate between that giving *sulphazate* and that giving *basic sulphazotate*, it sometimes happened that the solution set to a starch-like jelly instead of crystallising. He obtained a similar jelly by cooling a hot concentrated solution of *sulphazate* and *sulphazite*; also by boiling a solution of *sulphazate* and then cooling it. When strongly compressed, the jelly became a transparent, wax-like mass. Heated to  $50-60^\circ$  in this waxy state, it suddenly changed into a solution of *sulphazite* and minute crystals of *basic sulphazotate*. In all other respects, it proved to be intermediate in properties between *sulphazate* and *sulphazite*. No other *metasulphazates* could be prepared from it, so that Fremy was disposed to regard it as being a double salt of *sulphazate* and *sulphazite*. Its constitution must therefore have been that of nitrite combined with normal, or  $5/6$  normal hydroximidosulphate in such proportions and with such additions, perhaps, of alkali as prevented crystallisation.

We have not had Fremy's success in getting this salt in the jelly and wax-like forms, but have met with just such phenomena when forming barium sodium hydroximidosulphate,  $\text{BaNaNS}_2\text{O}_7 \cdot \text{H}_2\text{O}$ , as will be found described in our paper already frequently referred to. We have, however, obtained a salt, or homogeneous mixture of salts, of the same composition as the *metasulphazate*, but with the form of the silky, radiating, fibrous crystals of the nitrito-normal hydroximidosulphate, from which it differed only in showing deficiency of nitrite, that is, it was equivalent in composition to a mixture of the normal salt and its nitrite compound, both of which crystallise in the same habit. We give below Fremy's numbers, our own, and those calculated for the expression,  $3(\text{KNO}_2, 2\text{K}_3\text{NS}_2\text{O}_7, 4\text{H}_2\text{O}), \text{K}_3\text{NS}_2\text{O}_7, 3\text{H}_2\text{O}$ .

	Potassium.	Sulphur.	Nitrite.	Alk. potassium.
Found (Fremy) ...	35.10	16.74	4.81	— per cent.
„ (D. and H.)	35.10	16.68	—	10.47 „
Calculated .....	35.06	16.74	5.23	10.23 „

We prepared the salt by dissolving the hydroximidosulphate in hot concentrated nitrite solution containing alkali. To 100 c.c. of water, there were present  $45\frac{1}{2}$  grams of nitrite and  $1\frac{2}{3}$  grams of potassium hydr-

\* Often designated *metasulphazotate* in the French original, but not in the German translation.



oxide; for 66 mols. nitrite there were dissolved 10 mols. anhydrous normal hydroximidosulphate. Except for the salt being in beautiful, asbestos-like fibres, there was nothing to distinguish it from the jelly and the wax-like *metasulphazate*, which therefore we do not hesitate to class as a nitrito-hydroximidosulphate.

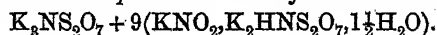
*Basic sulphazotate*, which Fremy considers next, has been shown by us already (*loc. cit.*) to be the  $5/6$  normal hydroximidosulphate, and not the salt of a distinct acid, the *sulphazotic*. It is liable to contain a small excess of potassium when crystallised from a strongly alkaline solution. A solution of the normal salt readily deposits it, as does also that of the nitrite compound of the normal salt.

*Neutral sulphazotate* was shown by Raschig to be the  $2/3$  normal hydroximidosulphate. Fremy distinguished the *potassium sulphazotates* from the salts previously described by him by their ability to form other sulphazotates by double decomposition. Fremy's analytical results in the case of the *neutral sulphazotate* are hopelessly out of accord with its constitution and properties, although those for the *basic sulphazotate* are satisfactory enough.

*Sulphazidate*, produced by the hydrolysis of the *sulphazotate*, is hydroxyamidossulphate (Claus). *Sulphazilate* and *metasulphazilate*, oxidation products of the *sulphazotate*, are  $\text{ON}(\text{SO}_3\text{K})_2$  and  $\text{ON}(\text{SO}_3\text{K})_3$ , and have been studied by Claus, Raschig, and Hantzsch.

*Metasulphazotate*.—Sometimes Fremy isolated a salt in the form of spangles (*paillettes*), in appearance like minute crystals of basic sulphazotate, but differing from them in not being hard. This salt he named, therefore, *metasulphazotate*. According to him, it can also be obtained by mixing (hot) solutions of the (*basic*) *sulphazotate* and *sulphazite*. It is very soluble in water, very alkaline, and unstable unless the water contains alkali. In pure water, it becomes *basic sulphazotate* and *sulphazite* again. It shows the greatest analogy to *metasulphazate*, and is distinguished from *basic sulphazotate* in the same way. It may be a compound of *basic sulphazotate* and *sulphazite*. So far Fremy. It will be evident that there is nothing in its history or properties to distinguish it, except its occurring in the form of sparkling particles, and even that can be met with in the *basic sulphazotate* suddenly precipitated; we have also obtained other of the sulphazotised salts in what may be called spangles, although not this particular salt. In the preceding paper (p. 434), we have described an impure form of nitrito- $2/3$  normal hydroximidosulphate, obtained by dissolving the  $5/6$  normal salt in a hot concentrated solution of nitrite, but still not so concentrated as to give the nitrito- $5/6$  normal double salt. This preparation is lustreless while in its mother liquor, but when dried on a tile has a fine silvery lustre. Thus, when dried in a desiccator,

exactly the composition of Fremy's *metasulphazotate*, and is much less alkaline than the *metasulphazate*. It may be formulated as



	Potassium.	Sulphur.	Nitrite.	Alk. potassium.
Found (Fremy).....	33.8	18.6	3.5	— per cent.
„ (D. and H.).....	33.79	18.35	—	1.09 „
Calculated.....	33.68	18.37	7.63	1.12 „

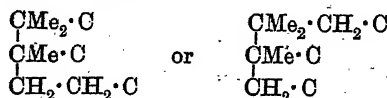
*Sulphammonate* and *sulphamidate* are respectively *nitrilosulphate* and *imidosulphate* (Berglund).

### XLV.—*Camphonic, Homocamphoronic, and Camphononic Acids.*

By ARTHUR LAPWORTH and EDGAR M. CHAPMAN, Salter's Fellow in the Research Laboratory of the Pharmaceutical Society.

IN a recent paper by one of us (Lapworth, Trans., 1899, 75, 1134), it was shown that when  $\alpha$ -dibromocamphor is warmed with moist silver or mercurous salts, about 15 per cent. of the substance is converted into bromocamphorenic acid, an unsaturated closed-chain compound, first prepared by Forster (Trans., 1896, 69, 46), who obtained it from the same source, but by a less direct method. The observation that the acid could be obtained by the new process was thought to be of much value, as it was thus rendered certain that the relationship subsisting between the structure of the acid and that of the parent compound must be of a comparatively simple character, and all ambiguity concerning the relative position of the bromine atoms in the two substances was removed: a point which had previously been involved in considerable doubt.

The results obtained during an investigation of homocamphoronic acid (Lapworth and Chapman, Trans., 1899, 75, 990), the oxidation product of bromocamphorenic acid, show conclusively that the latter substance contains the complex

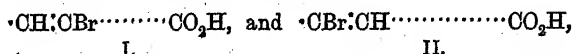


It was thought highly probable also that bromocamphorenic acid contained the group  $\cdot \text{CBr} \cdot \text{CH} \cdot$  as part of the closed chain, and the evidence bearing upon this point has already been discussed in detail (Lapworth, *loc. cit.*). Furthermore, the assumption was made that, of

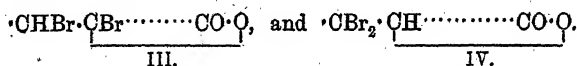
the pair of carbon atoms united by the ethylene linking, the one to which the bromine is attached is the nearer to the carboxyl group, but as the reasons for this supposition were not explicitly stated, they may be briefly indicated before entering into the evidence we have subsequently obtained.

The constitution of the oxidation product of bromocamphorenic acid shows that the latter must be either a  $\gamma\delta$ -, or a  $\delta\epsilon$ -unsaturated acid. The formation of a lactone ring would occur most readily at the  $\gamma$ -position in the former and at the  $\delta$ -position in the latter, that is to say, at the carbon atom which is nearest to the carboxyl group.

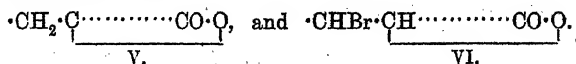
The two possible modes of representing bromocamphorenic acid, with regard to the relative positions of the bromine atom and the carboxyl group, may be thus expressed :



and the corresponding formulæ for dibromocampholide, its bromination product, are therefore,



Homocamphorenic acid, however, can be converted into a lactone by treating it with sulphuric acid, when it undergoes the isomeric change characteristic of this type of acid, yielding  $\alpha$ -monobromocampholide, the constitution of which may also be written in two different ways, corresponding with the alternative formulæ for bromocamphorenic acid, thus :



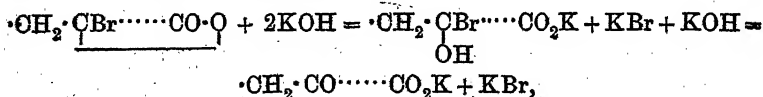
The two lactones, dibromocampholide and  $\alpha$ -monobromocampholide, however, exhibit certain noteworthy differences ; thus the former is reduced with the greatest ease to bromocamphorenic acid, whilst the latter, under far more energetic treatment, remains quite unchanged. The bromine atom of  $\alpha$ -monobromocampholide thus has properties entirely different from those of one of the two atoms in dibromocampholide, and it is probably therefore in a different position ; since, however, its position is necessarily identical with that of the other bromine atom of the latter, it follows that the two bromine atoms in dibromocampholide are probably attached to different carbon atoms, and the formulæ marked III and V are clearly in accordance with this conclusion.

Further evidence in favour of formula I is afforded by the fact that when camphorenic acid itself is brominated it yields  $\beta$ -monobromo-

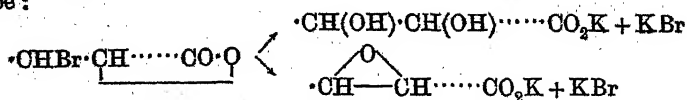
campholide, a lactone isomeric with  $\alpha$ -monobromocampholide. On the basis of formula I, the constitution of this substance may be represented as  $\cdot\text{CHBr}\cdot\text{CH}\cdots\cdots\text{CO}\cdot\text{O}$ , whilst if formula II be employed, the formulæ of the two lactones are identical, unless it be assumed that one is a  $\gamma$ - and the other a  $\delta$ -lactone, an assumption which it seems impossible to justify.

The foregoing mode of reasoning, however, did not appear to be altogether unassailable, and in order to obtain unequivocal evidence on this point, we have studied the behaviour of  $\alpha$ -monobromocampholide towards hydrolytic agents, and we have again to express our thanks to Dr. Forster who kindly consented to our carrying on investigations in this direction. The point appeared particularly interesting, as the above conclusions lead to the inference that the formation of dibromocampholide by the action of fuming nitric acid on  $\alpha$ -dibromocamphor is not merely one of oxidation, but is due to initial hydrolysis with formation of bromocamphorenic acid, which is then attacked by the bromine liberated during the reaction.

In a substance having the structure V above given for  $\alpha$ -monobromocampholide, hydrolysis of the lactone ring would be expected to result in the immediate formation of a ketonic acid in accordance with the change thus expressed :



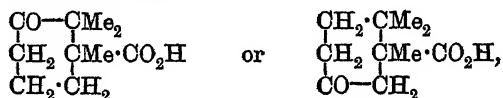
whilst if formula VI were the true one, a dihydroxy-compound would be the final product, or possibly an acid having a ring of the oxide type :



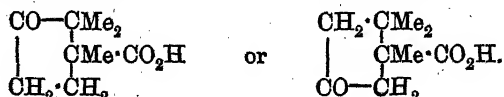
Forster boiled  $\alpha$ -monobromocampholide with baryta water and obtained a barium salt of the formula  $(\text{C}_{10}\text{H}_{15}\text{O}_3)_2\text{Ba}$ ; he describes the appearance, solubility, and melting point of the acid he obtained from it, but does not state that the acid was analysed or closely investigated (*loc. cit.*). We have carried out the hydrolysis with potash and find that the acid has the formula  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , as he supposed, and exhibits all the properties of a  $\gamma$ - or  $\delta$ -ketonic acid. Thus it gives a crystalline oxime and semicarbazone, and unites with hydrogen cyanide; it also gives a phenylhydrazone and *p*-bromophenylhydrazone, but these two derivatives, curiously enough, show no tendency whatever to assume a crystalline form, even when prepared from the pure acid and purified with extreme care; they give,

however, crystalline sodium salts, analyses of which indicate that they are derived from the respective hydrazones.

We think it advisable to distinguish this acid by a definite name, and propose to use the term *camphonic acid*, as the substance is isomeric with pinonic acid. Its constitution is doubtless very similar to that of camphononic acid, and, in accordance with the views already expressed by one of us (Lapworth, *loc. cit*), will probably be represented by the formula :

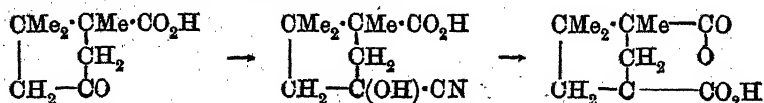


according as camphonic acid proves to have the structure,



In view of the close resemblance between the probable formulæ of these two acids, we have carried the study of camphonic acid into considerable detail, as we expected that the experience thereby gained would be of great service in the further study of camphononic acid, for the former is not difficult to prepare in quantities of 40—50 grams, whilst the latter can be obtained only in very small amount.

The point which from the first we regarded as worthy of the closest attention, was the behaviour of the ketonic acids towards hydrogen cyanide. In the case of camphononic acid, which, as we have shown, probably differs from camphoric acid only by the presence of the group :CO in place of :CH·CO<sub>2</sub>H, we hoped that it would be possible to effect a partial synthesis of camphoric acid in a very simple manner. It was to be expected that camphononic acid would combine with hydrogen cyanide, and that the hydroxynitrile thus formed would afford camphanic acid in accordance with the following scheme, using Perkin's formula for camphoric acid.

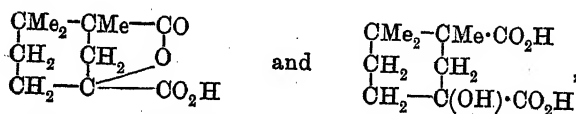


Our preliminary experiments on the subject showed that camphonic acid, if it united with hydrogen cyanide at all, would do so only under exceptional conditions, and we therefore turned our attention to its homologue, in order to ascertain what would probably be the most suitable mode of procedure. It was soon found that camphonic acid, unlike its homologue, combined readily with hydrogen cyanide, the most suitable conditions being those recommended by Haller and

Held (*Ann. Chim. Phys.*, 1891, [vi], 23, 145), in which a temperature of about  $-10^{\circ}$  is maintained during the whole of the preliminary stages.

On treating the product obtained by this means from camphonic acid with hydrochloric acid, a mixture of unaltered camphonic acid with two new substances was obtained; the separation of the three substances was easily effected, however, and of the new compounds that formed in the larger amount was a lactonic acid having the formula  $C_{11}H_{16}O_4$ , whilst the other, present only in small quantity, was a dibasic acid of the formula  $C_{11}H_{18}O_5$ .

The difference between these two substances is almost certainly due to stereochemical causes, the one being probably the lactone of a hydroxy-*trans*-dicarboxylic acid, and the other a hydroxy-*cis*-carboxylic acid. The formulæ for the two acids may be represented as follows:

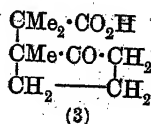
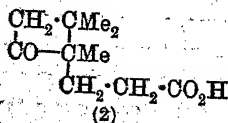
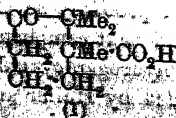


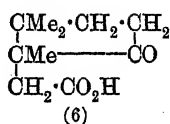
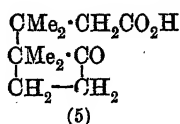
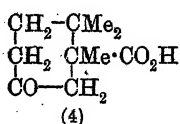
in which, it may be remarked, the choice of a formula for camphonic acid has been guided by circumstances to which allusion will shortly be made.

Returning to camphonic acid, we found that, even under conditions which were very favourable in the case of its homologue, no evidence of any tendency to combine with hydrogen cyanide could be obtained, and in almost every case we have been able to recover practically the whole of the camphonic acid; even anhydrous prussic acid produced no effect after several months contact with the ketonic acid, and, on evaporation, the whole of the camphonic acid was deposited in beautiful, transparent crystals.

The action of bromine upon the two ketonic acids was next studied, with a view to ascertaining, if possible, whether the acids contained the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$  or  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot$ . From analogy to the behaviour of acids and ketones of known structure, treatment with bromine at low temperatures would be expected, in the former instance, to afford a dibromo-acid, and, in the latter, a tetrabromo-acid.

From the two possible formulæ of homocamphoric acid, bearing in mind the considerations already alluded to, only six formulæ for camphonic acid are possible, namely:





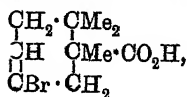
of which (1) and (4) are preferable, for the reasons mentioned in the case of bromocamphorenic acid (Trans., 1899, 75, 1139), namely, that these are the only two expressions which appear to be related in any simple manner to possible formulæ for  $\alpha$ -dibromocamphor; apart from this fact, however, no evidence against the others was adduced.

In these formulæ, it will be noticed that in one only, namely, (4), is there a  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot$  group, hence, if a tetrabromo-derivative of camphonic acid is readily obtainable, it would seem to follow that this one is the most probable of all, as the others are capable of affording dibromo-derivatives only.

It was found that by treating a solution of camphonic acid in chloroform with bromine, a dibromo-compound was readily obtained. This behaved in a somewhat curious manner, as it was not soluble in aqueous sodium carbonate, even on warming, but dissolved readily in dilute sodium hydroxide; the solution in the latter, when warmed, at once deposited a neutral compound, identical with the residue obtained when attempts were made to dissolve the dibromo-compound in hot sodium carbonate solution. The neutral substance was a lactone, and had the formula  $\text{C}_{10}\text{H}_{18}\text{O}_3\text{Br}$ , so that the original dibromo-compound was evidently a dibromo-acid, the sodium salt of which readily lost sodium bromide. This observation shows conclusively that the bromine atom is in the  $\gamma$ - or  $\delta$ -position, or, in other words, that the  $\text{CH}_2$  group in the  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  complex of camphonic acid must be in the  $\gamma$ - or  $\delta$ -position, a fact which completely excludes the formulæ numbered (2) and (5) in the above list.

When camphonic acid in the dry state is gently warmed with excess of bromine, a substance having the formula  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{Br}_3$  is obtained, which is neutral, but dissolves in hot aqueous caustic potash with production of a salt; it is therefore a lactone, and must be derived from a tetrabromo-acid,  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{Br}_4$ .

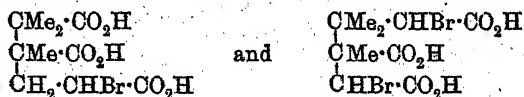
Unless, therefore, it can be established that some curious alteration in structure has occurred during the bromination, a very remote possibility, we no longer feel justified in maintaining that the choice of a formula made by one of us for bromocamphorenic acid (Trans., 1899, 75, 1139) is in complete accordance with the facts, and are compelled to regard the second formula given in the same paper, namely,



as the correct one; this is the only expression capable of explaining the behaviour of camphonic acid on bromination, and reference to the original paper will show that no positive evidence against it was adduced. Much careful work, however, will be required before it can be established with absolute certainty, and as we desire to reserve the further investigation of this interesting bromolactone, we think it advisable to make a statement of the results already obtained.

In the case of camphononic acid, the only product which could be isolated after treatment with bromine was a well characterised neutral substance which did not dissolve in the strongest alkalis, even after prolonged heating, and on analysis gave numbers which agreed most closely with the formula  $C_8H_6Br_4$ . This substance probably belongs to the aromatic series, and it appears not unlikely that it is a tetrabromoxylene, since the closely related camphoric acid is known to afford derivatives of metaxylene by the action of iodine, that is to say, under conditions not widely different from those employed in the present instance. As a knowledge of the exact structure of this substance could not be expected to throw any light upon the constitution of camphoronic acid, its investigation was not continued.

In connection with the structure of the substances under investigation, the behaviour of homocamphoronic acid towards bromine was investigated. If the two possible formulæ for this substance are examined, it will be seen that, in accordance with Volhard's rule, a monobromo- or a dibromo-compound derivative respectively should be produced. Moreover, in the resulting bromo-compounds,



the former or its ethyl ester would probably lose hydrogen bromide under suitable conditions, yielding an unsaturated substance, whilst in the latter compound there is no hydrogen in the  $\beta$ -position, and the formation of an unsaturated acid is impossible unless a further breaking down of the molecule occurred. Unfortunately, homocamphoronic acid resembles camphoronic acid in its behaviour towards bromine, and, although attacked by it at high temperatures, much charring occurs, and the product consists, for the most part, of unaltered acid mixed with readily soluble substances which do not contain bromine, and are probably hydroxy-acids or products of more profound alteration. Bredt succeeded in obtaining a brominated camphoronic chloride by heating the anhydrochloride with bromine at high temperatures, but in the case of homocamphoronic acid the anhydrochloride cannot be obtained in a pure form, as it undergoes decomposition when distilled, even in a vacuum, and is otherwise extremely unstable.



Attempts were made to obtain an unsaturated acid by heating bromocamphoronic chloride, or bromide with bromine, pouring the product into alcohol, and heating the bromo-ester thus formed with diethylaniline. The bromo-ester, however, charred when distilled in a vacuum, and nothing but a small quantity of triethyl homocamphorionate could be isolated. The crude, undistilled ester certainly lost hydrogen bromide on treatment with diethylaniline, and the resulting mixed acids decolorised permanganate, but as the substances themselves could not be isolated, no value can be attached to this observation.

An interesting result was obtained on leaving the anhydro-chloride of homocamphoronic acid to absorb moisture, as the product thus obtained was isomeric with the anhydrohomocamphoronic acid already described by us, and melted at  $128^{\circ}$  instead of at  $84^{\circ}$ . It is not easy to understand the true relationship of the two anhydro-acids, as the new substance gave a homocamphoronic acid identical in properties with that from which it had been obtained, and the anilic and paratolilic acids derived from the two anhydro-compounds were also identical; their relationship is probably the same as that subsisting between the two modifications of bromoanhydrocamphoronic acid.

The problem of the constitution of the derivatives of camphoronic acid was attacked in yet another direction. The oxime of camphononic acid was treated with sulphuric acid in the hope that it might undergo isomeric change resulting in the scission of the ring at a position not identical with that at which it opens during the formation of camphoronic acid, as such an occurrence would probably throw much light on the constitution of camphononic acid and, indirectly, of homocamphoronic and bromocamphoronic acids. During the process, the oxime was completely altered and a considerable quantity of an acidic substance containing nitrogen was isolated, but as this substance afforded a large quantity of camphoronic acid on oxidation, it was clear that the desired result had not been obtained, and the investigation of the substance was accordingly abandoned.

As the study of homocamphoronic acid and camphononic acid does not seem likely to throw further light upon the question of their constitution, we have decided to publish the results obtained with them, and to confine our attention to camphonic acid, which is much more easily dealt with and already promises to do much towards clearing up the questions involved in this and in the previous papers on the subject.

## CAMPHONIC ACID.

*Preparation of Camphonic Acid*,  $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CO} - \text{CH}_2 \end{array} \text{CMe} \cdot \text{CO}_2\text{H}$ .

$\alpha$ -Monobromocampholide (10 grams), prepared by treating bromo-camphorenic acid with sulphuric acid, is placed in a flask and covered with a solution of potassium hydroxide (6.8 grams) in water (20 c.c.); the whole is heated nearly to boiling with constant shaking until a clear liquid is obtained, which is cooled and filtered. Excess of hydrochloric acid is then added, when camphonic acid separates as a colourless oil, which on standing overnight solidifies; the whole of the crystalline material is separated by filtration, washed with a little water, dried, and may be purified by crystallisation from a mixture of ethyl acetate and light petroleum. About 6 grams of acid are thus obtained, and a further quantity may be isolated from the mother liquors by extraction with ether. A specimen purified in this way was dried at  $130^\circ$  and analysed:

0.2296 gave 0.5472  $\text{CO}_2$  and 0.1769  $\text{H}_2\text{O}$ . C = 65.0; H = 8.5.

$\text{C}_{10}\text{H}_{16}\text{O}_3$  requires C = 65.2; H = 8.7 per cent.

Camphonic acid separates from a mixture of ethyl acetate and light petroleum in the form of fairly large, flattened prisms with very poorly developed faces: it may also be obtained from water in fairly large crystals, and does not exhibit the tendency, shown by camphononic acid, to form fern-like aggregates under these conditions. The crystals are doubly refracting, and show straight extinction, whilst crushed fragments, examined in convergent polarised light, show, here and there, a biaxial interference figure of fairly wide angle and negative double refraction; the double refraction is strong and the dispersion weak. When melted beneath a cover-slip, it solidifies to a semitransparent mass, probably of a second modification which appears to be isotropic, or very weakly doubly refracting, and no very definite mode of crystal growth can be distinguished. The sublimed acid solidifies in fern-like crystals, with rounded terminations, exactly resembling the forms obtained from camphononic acid in similar circumstances.

The acid dissolves sparingly in cold, but fairly readily in hot water, separating from a saturated hot solution as an oil which slowly solidifies; it is readily soluble in methyl or ethyl alcohol, ethyl acetate, acetone, chloroform, or benzene, but is nearly, or quite insoluble in light petroleum.

When heated slowly, camphonic acid fuses at  $194^\circ$ , a slight amount of sublimation occurring; if, however, a crystal is heated in a capillary

tube, it is occasionally found that fusion does not occur at this point, but that the crystal settles down to an opaque, camphor-like mass, and afterwards melts at  $198^{\circ}$ . This phenomenon, which is not invariably to be observed, would appear to confirm the conclusion that the acid is dimorphous.

Camphonic acid, dissolved in chloroform, does not instantaneously discharge the colour of a dilute solution of bromine in the same liquid, and the colour of a solution of potassium permanganate is not at once discharged by a cold solution of the sodium camphonate, although in both cases rapid decolorisation takes place on heating; the acid is therefore a saturated compound. It is slowly oxidised by hot dilute nitric acid, doubtless with formation of homocamphoronic acid, and rapid oxidation occurs if the strong acid is employed.

The *oxime*,  $\text{CO}_2\text{H}\cdot\text{C}_9\text{H}_{15}\cdot\text{N}\cdot\text{OH}$ , was made by warming together 2 grams of the acid with 1.2 grams of caustic soda and 0.9 gram of hydroxylamine hydrochloride for half an hour on the water-bath; on neutralising with hydrochloric acid, a bulky, plastic mass separated, which was collected by means of a glass rod, and triturated with methyl alcohol, when it became pulverulent, and dried readily on a porous tile. It was purified by crystallisation from dilute methyl alcohol, and, after drying at  $100^{\circ}$ , was analysed:

0.1421 gave 0.3148  $\text{CO}_2$  and 0.1129  $\text{H}_2\text{O}$ .  $\text{C}=60.3$ ;  $\text{H}=8.8$ .

$\text{C}_{10}\text{H}_{17}\text{O}_3\text{N}$  requires  $\text{C}=60.3$ ;  $\text{H}=8.6$  per cent.

It dissolves very readily in ethyl acetate, acetone, methyl or ethyl alcohol, hot benzene, or chloroform, but is insoluble in light petroleum; it is nearly insoluble in water, but dissolves readily in dilute aqueous sodium carbonate or hydrochloric acid. It shows little tendency to separate in distinct crystals from any of these solvents, but crystallises from dilute methyl alcohol in very slender, short needles; large crystals, however, could not be obtained. It melts at  $125\text{--}127^{\circ}$ , and does not solidify on cooling.

When the oxime is covered with acetic anhydride containing a trace of sulphuric acid, the liquid becomes hot; but the product, as in every case where attempts were made to induce the occurrence of the Beckmann change, showed no tendency whatever to crystallise.

The *semicarbazone*,  $\text{CO}_2\text{H}\cdot\text{C}_9\text{H}_{15}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , was prepared by warming the acid with semicarbazide acetate in aqueous solution; it separates almost immediately as a flocculent mass of fine needles. It dissolves readily in acetic acid, but only sparingly in acetone, or methyl or ethyl alcohol, and very sparingly in water or ethyl acetate. The only medium from which it may be easily crystallised is methyl alcohol, from which it slowly separates in small crystals.

which melt and decompose at  $222-223^{\circ}$ ; these are usually distinct, flattened needles, the terminations of which are composed of two small faces, intersecting one another at about  $115^{\circ}$ ; the extinction is straight. Through the faces of some of the crystals, the (probably acute) bisectrix of a biaxial interference figure may be made out in convergent, polarised light, and emerges normally to the field; the axial angle is wide, and the double refraction is strong. After drying at  $100^{\circ}$ , the substance was analysed, with the following result:

0.2521 gave 0.5052  $\text{CO}_2$  and 0.1902  $\text{H}_2\text{O}$ .  $\text{C}=54.6$ ;  $\text{H}=8.4$ .

$\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}_3$  requires  $\text{C}=54.8$ ;  $\text{H}=7.9$  per cent.

The *phenylhydrazone* and *p-bromophenylhydrazone* of camphonic acid are precipitated immediately on mixing aqueous solutions of pure camphonic acid and the corresponding hydrazine acetates; if precipitated in the cold, they form pulverulent, white masses, which may be dried on porous earthenware and preserve their pulverulent character, but if touched with organic solvents, they at once become oily, and in no circumstances could afterwards be induced to exhibit a crystalline character. They dissolve to clear solutions in dilute aqueous sodium carbonate, carbon dioxide being evolved, and are reprecipitated on addition of acetic acid. Both yield sodium salts which crystallise fairly readily in small, flattened needles.

The sodium salt of the phenylhydrazone, dried at  $110^{\circ}$ , was analysed, with the following result:

0.3727 gave 0.0898  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=7.8$  per cent.

$\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}_2\text{Na}$  requires  $\text{Na}=7.3$  per cent.

The corresponding salt of the *p-bromophenylhydrazone* was also analysed:

0.4210 gave 0.0819  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=6.3$  per cent.

$\text{C}_{16}\text{H}_{22}\text{O}_3\text{N}_2\text{BrNa}$  requires  $\text{Na}=5.85$  per cent.

The hydrazones recovered from the carefully purified sodium salts were unaltered in properties, and therefore were not analysed.

#### *Action of Bromine on Camphonic Acid.*

*Dibromocamphonic acid*,  $\text{CBr}_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CO}-\text{CH}_2 \end{smallmatrix}\rangle\text{CMe}\cdot\text{CO}_2\text{H}$ .—When a few drops of bromine are added to a cold solution of camphonic acid in chloroform, no appreciable action occurs at first, but after the lapse of several minutes the colour disappears, hydrogen bromide is evolved, and on addition of more bromine, rapid action occurs, until two molecular proportions have been added. In one instance, 2 grams of the lactic acid, dissolved in 10 c.c. of chloroform, were left over-

night with bromine, when a crystalline mass was deposited; the liquid was evaporated by means of a current of air, the residue spread upon porous earthenware, and finally crystallised from chloroform. A specimen was analysed:

0.1708 gave 0.1884 AgBr. Br = 46.9.

$C_{10}H_{14}O_3Br_2$  requires Br = 46.7 per cent.

The dibromo-compound is very sparingly soluble in water or light petroleum, sparingly also in chloroform or benzene, but dissolves somewhat readily in methyl or ethyl alcohol, in warm ethyl acetate, and is very readily soluble in acetic acid. It crystallises from chloroform or hot dilute acetic acid in slender, glistening needles, from glacial acetic acid in prisms, and melts and decomposes at  $144^\circ$ . The small crystals from dilute acetic acid, when examined in polarised light, show straight extinction, and exhibit brilliant interference colours; the long axis of the crystals coincides with the direction of least elasticity.

The substance is so sparingly soluble in water that it appears to be insoluble in dilute aqueous sodium carbonate, and when the mixture is warmed alters its appearance, but does not dissolve; it dissolves readily, but apparently not entirely, in cold caustic soda, and if the solution is warmed, cloudiness ensues, followed by a deposition of the monobromolactone. If, however, it is boiled with excess of strong aqueous caustic soda, no such separation takes place, and on acidifying the resulting yellow solution, only a slight precipitate forms, although an oily acid may be extracted by means of ether. This substance has not, as yet, been closely examined.

Monobromocamphonolactone,  $CBr \begin{array}{c} \text{CH}_2 \cdot CMe_2 \\ \text{CO} - CH_2 \end{array} > CMe \cdot CO$ , is best pre-

pared in the following manner. To a solution of dibromocamphonic acid in about three times its weight of glacial acetic acid, rather more than one molecular proportion of sodium acetate is added, the whole boiled for several hours, evaporated nearly to dryness, water added, and the insoluble matter collected, dried, and crystallised from benzene. It is also obtained by boiling the acid with a strong solution of sodium carbonate. A specimen was dried at  $100^\circ$  and analysed:

0.1898 gave 0.1370 AgBr. Br = 30.7.

$C_{10}H_{13}O_3Br$  requires Br = 30.7 per cent.

Monobromocamphonolactone dissolves very readily in chloroform, acetic acid, ethyl acetate, or ethyl or methyl alcohol, less easily in cold benzene, and is insoluble in water or in light petroleum. It crystallises from benzene in beautiful, glistening needles or prisms, melts

at 110—111°, and fuses at the same temperature after solidification. When melted beneath a cover-slip on a microscope slide, it sets to a mass of very long, flat needles, separated from one another by considerable intervals; these, when examined in polarised light, have straight extinction, and show interference colours of the first and second order. As no axial figure was observed, the crystallographic characters of the crystals could not be determined; as viewed from above, the long axis of the needles coincides with the direction of greatest elasticity.

The lactone is quite insoluble in dilute aqueous sodium carbonate, or in cold dilute caustic alkalis; it slowly dissolves in hot, strong sodium hydroxide solution, however, losing hydrogen bromide, and doubtless yields the same oily acid as was obtained directly from dibromocamphonic acid by similar treatment.

*Tribromocamphonolactone*,  $\text{CBr} \begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CO} - \text{CBr}_2 \end{array} \text{CMe} \cdot \text{CO} \cdot \text{O} \text{---}$  When di-

bromocamphonic acid is gently warmed with excess of bromine, action readily occurs, hydrogen bromide being evolved, and is complete in 2 hours. The product may be purified by dissolving in chloroform and evaporating to dryness in order to get rid of hydrobromic acid, when the slightly viscid residue becomes crystalline on trituration with ether; it may be purified by drying on porous earthenware and crystallising from chloroform. The yield is nearly quantitative. On analysis:

0.1934 gave 0.2022  $\text{CO}_2$  and 0.0454  $\text{H}_2\text{O}$ . C=28.5; H=2.6.

0.2110 „ 0.2875 AgBr. Br=57.9.

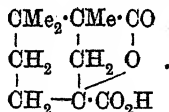
$\text{C}_{10}\text{H}_{11}\text{O}_3\text{Br}_3$  requires C=28.6; H=2.6; Br=57.3 per cent.

Tribromocamphonolactone dissolves fairly readily in chloroform, less readily in ethyl or methyl alcohol or benzene, and is insoluble in water and in light petroleum. It separates from chloroform in beautiful, white needles, melts at 166—167°, and, after solidification, melts at the same temperature. When melted beneath slips of glass, it solidifies in long, flat needles, in which no axial figures can be distinguished in convergent, polarised light; the extinction is straight, and the direction of greatest elasticity coincides with direction of greatest length.

It is not an acid, as is shown by the fact that it is not dissolved or altered by boiling with dilute solutions of sodium carbonate or hydroxide. When heated with strong alkalis, however, it dissolves fairly readily, losing much hydrogen bromide, and affords a yellow solution, which gives no precipitate on dilution and acidification.

*Action of Hydrogen Cyanide on Camphonic Acid.*

About 5 grams of camphonic acid were dissolved in about 50 c.c. of warm ether, and the whole cooled by means of a freezing mixture to  $-10^{\circ}$ ; 4 grams of finely powdered potassium cyanide were then introduced in small quantities at a time, and, finally, 3 c.c. of strong hydrochloric acid, drop by drop, care being taken throughout the whole operation to avoid any noticeable rise in temperature. After remaining for an hour at  $-10^{\circ}$ , the flask was allowed to stand for 48 hours at the ordinary temperature, when the ethereal layer was separated and allowed to evaporate spontaneously. A colourless, viscous oil remained, which was transferred to a flask, mixed with about 20 c.c. of strong hydrochloric acid, with which it was shaken at intervals during about 8 hours, and, in order that the reaction might be completed, was afterwards heated on the water-bath under a reflux condenser for a few hours. The liquid was then evaporated to dryness, the residue extracted, first with chloroform, and then with ethyl acetate, the remaining solid consisting of nearly pure ammonium chloride.

(1) *Isolation of the Lactone of the Hydroxy-trans-dicarboxylic Acid,*

—The chloroform extract was evaporated to dryness, dissolved in dilute acetic acid, and the resulting liquid allowed to evaporate spontaneously; a gradual deposition of a semi-crystalline material took place, which was removed, and freed from oily matter by spreading it on porous earthenware; it was finally purified by recrystallisation from dilute acetic acid, from which it separates as a mass of long, colourless needles.

The substance thus obtained contains water of crystallisation. When slowly heated, it aggregates together at  $100^{\circ}$ , gives off water, and finally melts at about  $140^{\circ}$ . The anhydrous substance is easily obtained by heating the crystals at  $150^{\circ}$  for 15 minutes and crystallising the residue from benzene. A specimen thus prepared was dried at  $100^{\circ}$  and analysed:

0.2147 gave 0.4894  $\text{CO}_2$  and 0.1439  $\text{H}_2\text{O}$ . C = 62.1; H = 7.4.

$\text{C}_{11}\text{H}_{16}\text{O}_4$  requires C = 62.3; H = 7.5 per cent.

The basicity of the acid was determined by titration against standard alkali, phenolphthalein being used as indicator. 0.1203 gram required

5.6 c.c. of  $N/10$  soda for neutralisation, giving the equivalent of the acid as 214, that required for a monobasic acid,  $C_{11}H_{16}O_4$ , being 212.

The anhydrous acid dissolves very readily in methyl or ethyl alcohol, acetic acid, ethyl acetate, or chloroform, and less readily in benzene; it is more sparingly soluble in water, and separates from hot saturated aqueous solutions as an oil, which solidifies on cooling to a mass of fine needles; it appears to be insoluble in light petroleum. It separates from benzene in silky, flat needles, which are terminated by faces making a very acute angle with one another; the extinction is straight. It melts sharply at  $144-145^\circ$ , this also being the melting point of the substance after solidification.

When fused between slips of glass, it sets, if the cooling is rapid, to a glassy mass broken up by cracks due to the considerable contraction, but if the glass be carefully warmed, the whole gradually changes to a number of fan-like structures, which, in polarised light, show large, transparent patches exhibiting aggregate polarisation; in convergent polarised light, the interference figure is usually that characteristic of a section parallel to the optic axial plane, but here and there the bisectrix of an axial figure of wide angle emerges nearly perpendicular to the field.

When the acid is heated at its boiling point, it slowly decomposes, water and carbon dioxide being evolved. The product seems to contain an unsaturated acid, as its solution in dilute sodium carbonate at once discharges the colour of potassium permanganate. Moreover, a small quantity of a volatile, crystalline lactone also appears to be formed, and may be separated by boiling the product with water, when a sparingly soluble substance, having a camphor-like odour, distils over with the steam; this is insoluble in sodium carbonate. Owing to the great difficulty in obtaining these substances in sufficient quantity, their investigation was not pursued.

The *barium* salt was made by adding moist barium carbonate to a boiling aqueous solution of the acid. It was very soluble in water and crystallised in minute needles having very weak double refraction. It was dried at  $130^\circ$  and analysed :

0.3937 gave 0.1686  $BaSO_4$ .  $Ba = 25.2$ .

$(C_{11}H_{15}O_4)_2Ba$  requires  $Ba = 24.5$  per cent.

In accordance with its lactic character, the acid is capable of forming a second barium salt. This was obtained by boiling it with excess of baryta water for half an hour and then leading carbon dioxide into the boiling solution; the liquid was afterwards filtered and evaporated. The salt then obtained was more readily soluble in



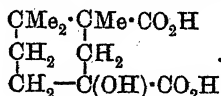
cold than in hot water, and was therefore precipitated from solution by addition of alcohol, separated by filtration, washed with dilute alcohol, dried at 150°, and analysed :

0.1416 gave 0.0893 BaSO<sub>4</sub>. Ba = 37.1.

C<sub>11</sub>H<sub>16</sub>O<sub>5</sub>Ba requires Ba = 37.5 per cent.

A dilute solution of the sodium salt, prepared by neutralising a cold aqueous solution of the acid with dilute sodium hydroxide, gave a buff precipitate with ferric chloride, a white precipitate with bismuth nitrate, but no precipitate with salts of barium, calcium, copper, mercury, manganese or chromium.

(2) *Isolation of the hydroxy-cis-dicarboxylic acid,*



—The ethyl acetate extract on evaporation deposited a small quantity of an acid in brilliant, compact crystals, which were purified by recrystallisation from hot ethyl acetate and analysed :

0.2017 gave 0.4230 CO<sub>2</sub> and 0.1431 H<sub>2</sub>O. C = 57.2 ; H = 7.9.

C<sub>11</sub>H<sub>18</sub>O<sub>5</sub> requires C = 57.4 ; H = 7.9 per cent.

The basicity of the acid was determined by titration against standard alkali in presence of phenolphthalein. A solution of 0.1250 gram required 10.8 c.c. of *N*/10 soda for neutralisation, hence the equivalent of the acid is 115.7, that required for a dibasic acid, C<sub>11</sub>H<sub>18</sub>O<sub>5</sub>, being 115.

The substance thus obtained is therefore a dicarboxylic acid. It resembles isocamphanic acid in being quite insoluble in chloroform ; it is insoluble also in benzene or petroleum, very sparingly soluble in water or in dry ethyl acetate, but dissolves somewhat freely in moist ethyl acetate and very readily in acetic acid, or in methyl or ethyl alcohol. It crystallises from ethyl alcohol in elongated, six-sided orthorhombic plates. When heated slowly, it aggregates together and finally melts with evolution of gas, doubtless water vapour, at 207°.

Unfortunately, the total quantity of this compound derived from a number of experiments was very small, so that positive proof of the presence of the hydroxyl group in the acid has not been obtained ; the occurrence of this group, however, is scarcely open to question when the mode of origin of the acid is taken into consideration.

The acid seems to be capable of forming an anhydride, as when melted it evolves gas, doubtless water vapour, and is afterwards readily soluble in chloroform or benzene, but insoluble in sodium

carbonate solution, although it dissolves slowly in hot sodium hydroxide.

A dilute solution of the sodium salt gave a light blue precipitate with copper sulphate, and a buff-coloured one with ferric chloride; with mercuric chloride, a white precipitate was obtained which increased in amount when the solution was boiled, whilst precipitates were also obtained with mercurous, lead, and bismuth salts, but none with nickel, cobalt, barium, or calcium salts. The lead salt is insoluble in moderately dilute acetic acid.

## II. HOMOCAMPHORONIC ACID.

### *Attempts to Brominate Homocamphoronic Acid.*

Homocamphoronic acid is apparently not affected by bromine at temperatures below  $140^{\circ}$ , but at this temperature rapid action occurs, and the product, which is at first oily, becomes crystalline when left in contact with water; the crystalline material, however, proved to consist very largely of unaltered homocamphoronic acid. No bromine was present in the solid material, so that it is probable that, like camphoronic acid, this acid affords a hydroxy-derivative, or lactonic acid, on treatment with bromine under these conditions. Similar results were obtained with the anhydro-acid.

Bredt succeeded in preparing a brominated anhydrocamphoronic acid by heating the anhydro-chloride with bromine in closed tubes, (*Annalen*, 1898, 299, 142). On attempting to prepare the anhydro-chloride of homocamphoronic acid by heating the anhydro-acid with chlorides of phosphorus, it was found that, on distillation in a vacuum, the product underwent considerable decomposition, and a pure compound could not be isolated. Attempts were made to brominate the mixture of anhydro-chloride and phosphorus oxychloride, but without success.

*Trimethyl homocamphoronate*,  $C_7H_{13}(CO_2Me)_3$ .—This substance was isolated during an experiment in which homocamphoronic acid had been heated with 3 molecular proportions of phosphorus pentabromide and the product poured into methyl alcohol. It was also made, for purposes of comparison, by warming the dry silver salt of homocamphoronic acid with methyl iodide. It formed a nearly colourless, slightly viscous liquid, which boiled with very little decomposition at  $305-308^{\circ}$  under atmospheric pressure. On analysis :

0.3378 gave 0.7023  $CO_2$  and 0.2515  $H_2O$ .  $C = 56.6$ ;  $H = 8.2$ .

$C_{15}H_{22}O_6$  requires  $C = 56.9$ ;  $H = 8.1$  per cent.

*Action of Phosphorus Trichloride on Anhydrohomocamphoronic Acid.*

*β*-Anhydrohomocamphoronic Acid,  $\text{CO}_2\text{H} \cdot \text{C}_7\text{H}_{13} \begin{smallmatrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{smallmatrix} \text{O}$ .

Anhydrohomocamphoronic acid was heated with excess of phosphorus trichloride until action ceased; the liquid was then poured off from the layer of phosphorous acid and the excess of trichloride removed by evaporation over a naked flame. The residue, which presumably contained anhydrocamphoronic chloride, gave nothing crystalline on distillation in a vacuum or on fractional precipitation from its benzene solution with petroleum; the residues from a number of experiments were united and exposed to the air, when deliquescence occurred, followed by a deposition of crystalline material; the whole was then spread on porous earthenware, dried and crystallised from benzene. It contained no chlorine and gave the following results on analysis:

0.2555 gave 0.5234  $\text{CO}_2$  and 0.1494  $\text{H}_2\text{O}$ .  $\text{C} = 55.8$ ;  $\text{H} = 6.5$ .

$\text{C}_{10}\text{H}_{14}\text{O}_6$  requires  $\text{C} = 56.1$ ;  $\text{H} = 6.5$  per cent.

This substance, which is isomeric with the anhydrohomocamphoronic acid already described (Trans., 1899, 75, 998), has properties which are not very different from those of the latter substance; it is less soluble in benzene or chloroform than is the  $\alpha$ -derivative, crystallises from benzene in well-defined plates or in short, flattened prisms, and melts at  $128\text{--}129^\circ$  when slowly heated.

The presence of a carboxyl group in the substance is shown by the fact that it dissolves rapidly in dilute aqueous sodium carbonate; it may be precipitated from this solution apparently unaltered if acid is at once added, but hydrolysis slowly goes on if the solution is allowed to stand.

The  $\beta$ -anhydro-acid behaves like its isomeride when heated, losing carbon dioxide and yielding camphononic acid, and the yield of the ketonic acid appears to be greater than in the latter case. In order to ascertain whether this compound was formed by a stereomeric alteration of the anhydrohomocamphoronic acid, it was boiled for some hours with water until hydrolysis was thought to be complete, and the resulting homocamphoronic acid examined, after crystallisation twice from water; the general properties of the acid appeared to be unaltered, but it was found that, after fusion, the solidified residue melted at  $126^\circ$ , whilst the original homocamphoronic acid after fusion and solidification invariably melted at  $86\text{--}87^\circ$  or thereabouts. The specific rotation of the acid in a 2 per cent. solution was  $[\alpha]_D - 10.16$ , a number almost exactly that given by the original acid. As the curious difference might be due to the presence of a small quantity of unaltered

$\beta$ -anhydro-acid, the whole was therefore boiled with excess of aqueous caustic soda for 10 minutes, and afterwards acidified ; the recovered acid then melted at  $87^{\circ}$  after fusion. The assumption that the phenomenon was due to the presence of a small quantity of the unaltered  $\beta$ -anhydro-acid does not, however, seem altogether satisfactory, as it was found that a mixture of the acid which behaved in this way with ordinary homocamphoronic acid melted after fusion and solidification at temperatures between  $87^{\circ}$  and  $127^{\circ}$ .

It was thought desirable to examine the action of bases upon the  $\beta$ -anhydro-acid. Portions were therefore dissolved in benzene and the solution mixed with aniline and paratoluidine respectively and the resulting anilic and paratolilic acids examined. They melted at  $98$ — $100^{\circ}$  and  $163$ — $164^{\circ}$  respectively, and had all the properties of the substances prepared from the  $\alpha$ -anhydro-acid. If the difference depends on the particular carboxyl groups involved, and not on stereochemical change, it would seem probable that one or other of the anhydro-acids, possibly the  $\beta$ -compound, is produced by the elimination of water from the adipic acid chain. Reference has already been made (Lapworth and Chapman, *Trans.*, 1899, '75, 990) to the probability that this change occurs as a stage in the formation of camphononic acid.

### III. CAMPHONONIC ACID.

The processes for the preparation and purification of this acid (Lapworth and Chapman, *loc. cit.*) may be considerably simplified with quantities of more than 5 grams by subjecting the crude product, obtained by heating homocamphoronic acid to slow fractional distillation. The portions of lower boiling point are oily, but afford a further small quantity of camphononic acid by repeated distillation.

On distilling large quantities of homocamphoronic acid, prepared by oxidising monobromocampholide, a very small quantity of a ketone boiling at  $203$ — $205^{\circ}$  is obtained. As this does not happen when camphononic acid is distilled, or pure homocamphoronic acid is employed, we have been forced to conclude that the crude homocamphoronic acid prepared in this way is not homogeneous, as was at first supposed (Lapworth, *loc. cit.*), and the formation of the ketone would appear to indicate that a small quantity of a substituted adipic acid is present in the product. Unfortunately, the quantity of this ketone formed was far too small to admit of close investigation ; thus 25 grams of crude homocamphoronic acid gave only 7.5 grams of camphononic acid and 0.6 gram of the ketone.

*Action of Hydrogen Cyanide on Camphononic Acid.*

Camphononic acid was subjected to the action of hydrocyanic acid under very different conditions. Thus, it was dissolved in ether and treated with potassium cyanide and hydrochloric acid at  $-10^{\circ}$  as recommended by Haller and Held (*loc. cit.*); it was also treated in closed tubes with strong and dilute hydrocyanic acid at temperatures varying from  $-10^{\circ}$  to  $110^{\circ}$ , for periods sometimes of several weeks, and in all cases was recovered almost quantitatively. In anhydrous hydrocyanic acid, the camphononic acid dissolved fairly readily; the solutions were heated or cooled for long periods without result, however, and in one instance the acid was recovered unchanged after being left with the anhydrous substance for 3 months at the ordinary temperature. It may be added that, in nearly all cases, the crude substance recovered was tested for nitrogen, and that in no case was more than a very small quantity detected.

*Oxime of Camphononic Acid,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{13}\cdot\text{N}\cdot\text{OH}$ .*

This oxime is easily prepared by warming camphononic acid with hydroxylamine hydrochloride and excess of sodium hydroxide in the usual manner. On adding hydrochloric acid to the alkaline liquid, the oxime is precipitated as a somewhat resinous, nearly colourless mass, which on trituration with methyl alcohol, becomes brittle and may be drained on porous earthenware. A specimen crystallised from methyl alcohol and dried at  $100^{\circ}$  until constant in weight, was analysed:

0.2566 gave 0.5437  $\text{CO}_2$  and 0.1928  $\text{H}_2\text{O}$ . C = 58.0; H = 8.4.

$\text{C}_9\text{H}_{15}\text{O}_3\text{N}$  requires C = 58.4; H = 8.1 per cent.

The oxime dissolves readily in hot ethyl or methyl alcohol, and also in ether, ethyl acetate, or acetone, but is less soluble in cold methyl alcohol, and is insoluble, or nearly so, in benzene or chloroform. It separates from a mixture of ethyl acetate and petroleum in beautiful, hard, shining prisms melting at  $177-178^{\circ}$ , but when crystallised by spontaneous evaporation of its solution in methyl alcohol, forms very large, well-developed, transparent rhombohedra, which are entirely different in crystalline form, and contain solvent of crystallisation, as they rapidly become opaque and diminish in weight on exposure to the air. These crystals, when slowly heated, appear to melt at the same temperature as the other forms, doubtless owing to rapid loss of methyl alcohol.

The substance is very sparingly soluble in water, even when hot, but dissolves in dilute sodium carbonate solution, and is reprecipitated

from the solution, on addition of acids, as a voluminous mass of microscopic needles, which redissolves on addition of excess of acid.

The oxime dissolves in warm concentrated sulphuric acid, and only slight charring occurs. In one case, 4 grams of the oxime were warmed for an hour with the strong acid at 90—95°, the product, on cooling, poured into water, and the sulphuric acid eliminated as usual with baryta water; the barium in the filtrate was then precipitated exactly with dilute sulphuric acid, and the clear solution, after evaporation nearly to dryness, left in a cool place for several days. About 2½ grams of an acid slowly separated in well-formed prisms, which were recrystallised from a little water, in which the substance was readily soluble. The compound thus obtained was homogeneous and contained nitrogen, and as it was entirely different in character from camphononic acid or its oxime, was probably a product of intramolecular change of the latter. In order to determine whether its further investigation was desirable, it was boiled with dilute nitric acid for about 70 hours, the liquid evaporated, freed from nitric acid in the usual way, dissolved in water, and boiled with excess of baryta water, when a considerable quantity of an insoluble barium salt was precipitated; the acid liberated from this yielded about 0.7 gram of nearly pure camphoronic acid, and for the reason stated in the introductory portion of the paper, this line of investigation was not pursued.

#### *Action of Bromine on Camphononic Acid.*

When dry bromine is added to a cold solution of camphononic acid in chloroform, no appreciable action occurs at first, but in the course of a few hours hydrogen bromide is evolved, and a considerable quantity of bromine eventually disappears. On evaporating the solution after excess of bromine has been added, an oily residue remains which may be separated into two portions by means of sodium carbonate. The acidic portion yields very little crystalline matter until subjected to further bromination, but the neutral part gradually becomes crystalline when triturated with cold strong formic acid. The crystalline substance may be purified by draining on porous earthenware and crystallising from hot acetic acid. A specimen dried in a vacuum was analysed, with the following results:

0.1691 gave 0.1370 CO<sub>2</sub> and 0.0289 H<sub>2</sub>O. C = 22.5; H = 1.8.

0.1966 „ 0.3486 AgBr; Br = 75.4.

C<sub>8</sub>H<sub>8</sub>Br<sub>4</sub> requires C = 22.8; H = 1.4; Br = 75.8 per cent.

The substance is evidently formed from camphononic acid by loss of carbon dioxide and hydrogen. It is insoluble in water, and is not dissolved by boiling with strong aqueous potassium hydroxide. It

dissolves somewhat readily in most of the ordinary organic media except light petroleum. When crystallised from warm glacial acetic acid, it forms beautiful, colourless, lustrous needles or prisms, which melt sharply at 78°.

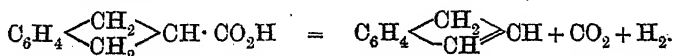
The bromo-compound readily loses bromine under the influence of moist sodium amalgam or zinc dust and acetic acid, but the products could not be isolated owing to the very small quantity of material at our disposal. When sodium amalgam is added to a solution of the substance in a mixture of acetic acid and alcohol, a beautiful magenta colour was frequently developed, but as this effect was not invariably produced, it was probably due to a small quantity of impurity in the bromo-derivative.

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### XLVI.—*New Syntheses of Indene.*

By F. STANLEY KIPPING, Ph.D., D.Sc., F.R.S., and HAROLD HALL, A.I.C.

THE hydrocarbon indene,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH} \end{smallmatrix} \text{CH}$ , which was first discovered in coal-tar and isolated with the aid of its compound with picric acid by Krämer and Spilker about ten years ago (*Ber.*, 1890, 23, 3279), was prepared synthetically some four years later by Perkin and Révay (*Trans.*, 1894, 65, 228), who obtained it by the distillation of hydrindene-carboxylic acid,



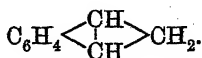
This synthetical method of preparation, and also the isolation of pure indene from coal-tar, appear, however, to be attended by considerable difficulty, and consequently, although there are many general methods known by which derivatives of indene may be obtained fairly easily, the preparation of the parent hydrocarbon in a state of purity is still a task of some magnitude.

This statement is equally true with regard to the hydrocarbon hydrindene, since the only method by which this substance has yet been prepared is by the reduction of indene with sodium and alcohol.

Under these circumstances, several attempts have been made to obtain these hydrocarbons from more convenient sources. König, for example, tried to prepare indene indirectly from  $\alpha$ -hydrindamine by distilling  $\alpha$ -hydrindyl alcohol with zinc chloride, but was unsuccessful (*Annalen*, 1893, 275, 341); somewhat similar experiments by Revis and

Kipping (Trans., 1897, 71, 238) also led to no result, in spite of the fact that in the latter case, the improved method of preparing  $\alpha$ -hydrindamine itself rendered this substance easily accessible.

Another matter which added to the interest attached to the preparation of the hydrocarbons in question was that brought prominently under notice by Perkin and Révay, namely, the possibility that the indene of coal-tar is not identical, but structurally isomeric with, the hydrocarbon obtained synthetically, as represented by the following formulæ :

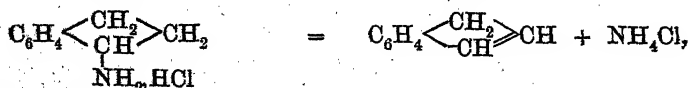


As a matter of fact, Perkin and Révay (*loc. cit.*), who directly compared the two preparations, came to the conclusion that they were not identical, although they had the same boiling point, and showed the same chemical behaviour, and the reasons for this conclusion were that the two preparations differed in density, and had different magnetic rotatory powers. On reduction, the two preparations appeared to be converted, as was to be expected, into one and the same hydrindene, but here, again, the physical properties of the two products were not identical, although less dissimilar than in the case of the two samples of indene.

It will be obvious from the above statements that the further investigation of indene, especially with regard to its physical properties, was desirable, and in this paper we make a small contribution to our knowledge of this hydrocarbon.

In the first place, we describe a new and simple method for the preparation of indene, a method which has enabled us to procure what we believe to be the pure hydrocarbon, in considerable quantities. Starting from cinnamic acid, we first prepare phenylpropionic acid, convert this compound into  $\alpha$ -hydrindone by the method previously described (Kipping, Trans., 1894, 65, 484), then prepare hydrindoxime, and reduce to  $\alpha$ -hydrindamine; in all these reactions, the yield is practically the theoretical one, except in the conversion of phenylpropionic acid into hydrindone, where it is only about 60 per cent. of the theoretical.

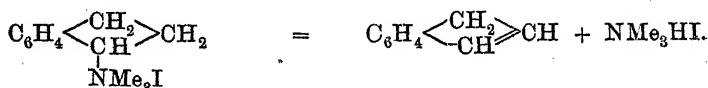
Dry hydrindamine hydrochloride is then heated at about 250°, when it rapidly decomposes into indene and ammonium chloride,



a reaction which is closely analogous to those which occur in the case of the hydrochlorides of dihydrocarvylamine,  $\alpha$ -thujonamine, and similar compounds; the yield seems to be nearly quantitative.



Trimethylhydrindamine iodide is also readily decomposed when it is submitted to dry distillation, giving indene and trimethylamine hydroiodide in almost theoretical quantities:



The indene obtained by these processes was carefully examined, and for reasons which are given later, we conclude that the hydrocarbons obtained by Krämer and Spilker (from coal-tar), by Perkin and Révay, and by ourselves represent one and the same chemical individual.

#### INDENE FROM HYDRINDAMINE HYDROCHLORIDE.

Pure hydrindamine hydrochloride (Revis and Kipping, *loc. cit.*, p. 250), in quantities of about 2 grams at a time, is placed in a test-tube which is then drawn out and bent at an angle. The salt is then carefully heated; at first it melts, but on heating more strongly an oil distils over, leaving behind a white substance which on further heating sublimes; this on examination proves to be ammonium chloride. The oil is washed with water and extracted with ether; the ethereal solution is then dried with calcium chloride, the ether distilled off, and the residue fractionated; the yield of the crude product is about 95 per cent. of the theory. In the first distillation, almost all the oil passes over between 181° and 182°, about 5 per cent. of residue remaining in the distillation flask. The portion boiling at 181–182° is then redistilled over metallic sodium and the main portion, which passes over at 181–181.3° under 749.6 mm. pressure collected, only a slight residue remaining in the flask.

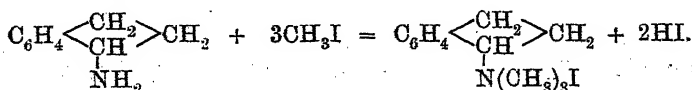
#### INDENE FROM TRIMETHYLHYDRINDAMINE IODIDE.

##### *Preparation of Trimethylhydrindamine Iodide.*

When 1 mol. of methyl iodide is treated with 1 mol. of hydrindamine in ethereal solution, trimethylhydrindamine is formed and not the monomethylhydrindamine as might be expected, a quantity of the hydrindamine being unacted upon. By using 3 mols. of methyl iodide to 1 mol. of the base, trimethylhydrindamine iodide can be obtained in almost theoretical quantities.

Pure hydrindamine (5 grams) is carefully dried over solid potash in ethereal solution, and after filtering is treated with an ethereal solution of methyl iodide (16 grams); the resulting mixture often rises in temperature sufficiently to cause the ether to boil, and, after some little time, a beautifully white, crystalline solid separates out; the ether is then distilled off, during which process the crystalline substance changes in colour, assuming a light red tint. The solid residue

is then dissolved in as small a quantity as possible of warm methyl alcohol, and dry ether is then added to the alcoholic solution. The quaternary salt is deposited in bulky masses of long needles, which rapidly change into thick prisms. These are pumped off, washed with ether, and placed on porous earthenware. The above reaction may be represented as follows:



On analysis, the following result was obtained:

0.3 trimethiodide, dried at  $100^\circ$ , gave 0.232 AgI.  $\text{I} = 41.8$ .

$\text{C}_{12}\text{H}_{13}\text{NI}$  requires  $\text{I} = 41.91$  per cent.

Trimethylhydrindamine iodide is fairly soluble in cold methyl alcohol, more readily on warming, and the solution deposits, on cooling, beautiful transparent, compact, six-sided prisms, and plates which melt and decompose at about  $198^\circ$ . It is insoluble, or nearly so, in petroleum and ether. On adding ether to its warm solution in methyl alcohol, the quaternary salt is precipitated as a very bulky, flocculent mass of needles; on standing, however, a remarkable change takes place, the flocculent mass passing into solution, and the salt being deposited in thick prisms. The substance, therefore, is dimorphous, and the change of the one crystalline form into the other can be easily observed under the microscope.

#### *Action of Heat on Trimethylhydrindamine Iodide.*

The quaternary compound, in quantities of about 2 grams at a time, is placed in a dry test-tube, which is then drawn out and bent at an angle; the substance is then carefully heated by means of a small flame. It first melts, but on heating more strongly an oil distils over, and there remains in the retort a red liquid, which, on cooling, solidifies to a crystalline mass. The oily distillate thus obtained is crude indene, the yield of which is theoretical. By fractional distillation, and finally by distillation over metallic sodium, the indene is obtained as a colourless liquid boiling at  $181^\circ$  under 749 mm. pressure.

#### *Examination of the Crystalline Residue.*

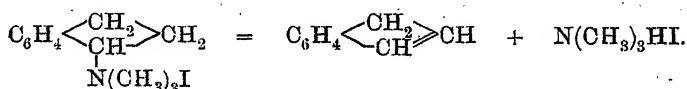
The substance proved to be trimethylamine hydriodide,  $\text{N}(\text{CH}_3)_3\text{HI}$ . It crystallised from water in needles melting at  $253^\circ$ , gave a yellow precipitate of silver iodide with silver nitrate, and when treated with caustic potash gave a strong basic odour; further, when treated with dilute hydrochloric acid and sodium nitrite, a dark precipitate of a periodide was formed. An iodine determination was made in a

sample which had been recrystallised twice from water and dried in a steam oven during 1 hour.

0.1350 gave 0.1679 AgI.  $I = 67.3$ .

$C_9H_{10}NI$  requires  $I = 67.8$  per cent.

These results show that on heating trimethylhydrindamine iodide, the following decomposition occurs:

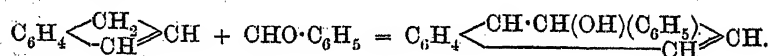


#### *Identification of the Hydrocarbon.*

For the identification of indene, which, according to Krämer and Spilker (*loc. cit.*), is very difficult to burn, we made use of its property of combining with picric acid and benzaldehyde.

*Indene Picrate.*—For the preparation of this compound, a solution of picric acid in benzene is treated with indene; after some time, golden-yellow needles of a picrate are deposited, and after recrystallising from benzene the product melts at  $98^\circ$ ; the melting point of indene picrate given by Krämer and Spilker is  $98^\circ$ .

Marckwald (*Ber.*, 1895, 28, 1500) has shown that indene behaves very like indole in some respects, and that it condenses very readily with benzaldehyde in presence of a small quantity of sodium ethoxide; he represents the reaction as follows:



The indene prepared from hydrindamine hydrochloride by the above method was treated with benzaldehyde as described by Marckwald, and the yellowish product which was thus formed was purified by repeated crystallisation from alcohol and also from a mixture of chloroform and petroleum; it was thus obtained in yellow crystals melting at  $133$ – $134^\circ$ ; Marckwald, who prepared this compound from a sample of coal-tar indene, gave  $135^\circ$  as the melting point. For analysis, a sample was dried over sulphuric acid.

0.109 gave 0.347  $CO_2$  and 0.0609  $H_2O$ .  $C = 86.6$ ;  $H = 6.2$ .

$C_{16}H_{14}O$  requires  $C = 86.4$ ;  $H = 6.4$  per cent.

These experiments seem to prove that the hydrocarbon obtained by us is identical with coal-tar indene. As further evidence, it may be mentioned that the synthetical product combines directly with bromine at the ordinary temperature, giving a heavy oil which, when boiled with dilute nitric acid, is gradually converted into a crystalline substance melting at  $131^\circ$ ; this substance is evidently identical with

the indene oxybromide described by Krämer and Spilker (*Ber.*, 1884, 17, 125). On prolonged oxidation with dilute nitric acid, the oxybromide is converted into an acid which melts above  $184^{\circ}$ , and when heated on a sand-bath, sublimes in long needles melting at  $128^{\circ}$ . These are the properties of phthalic acid.

*Identification of the Hydrocarbon with Perkin and Révay's Synthetical Indene.*

Having established the identity of our hydrocarbon with coal-tar indene, we were led to compare it with the synthetical compound prepared by Perkin and Révay. These authors state (*loc. cit.*) that their indene, like the coal-tar hydrocarbon, gave a reddish-brown resin (para-indene) on treatment with concentrated sulphuric acid, and that it also gave, with picric acid, a picrate very similar in properties to the picrate of the indene obtained from coal-tar. These statements seemed to leave the identity of the two preparations an open question, and, as already stated, the results of an examination of the physical properties led Perkin and Révay to the conclusion that the compounds were different. Under these circumstances, we made a series of determinations of the specific gravity of our hydrocarbon, in order to compare the results with those obtained by Perkin and Révay.

The indene used in these determinations was very carefully purified by repeated fractional distillation, first alone, then several times over sodium, and finally alone; it was thus obtained quite colourless, and having a constant boiling point of  $181-181.3^{\circ}$  under 749.6 mm. pressure, the thermometer thread being entirely surrounded by the vapour. The boiling point given by Perkin and Révay is  $180.5-181^{\circ}$  under 764 mm. pressure.

The specific gravity determinations were made as soon as possible after distillation, as the hydrocarbon becomes yellow on keeping; two different preparations were employed.

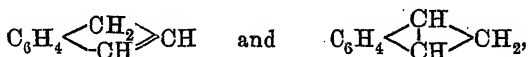
(1)  $d_{40}^{40} = 1.0079$  as the mean of three determinations.

(2)  $d_{40}^{40} = 1.0082$  " " "

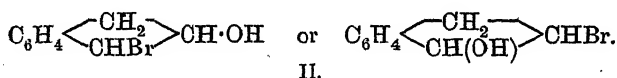
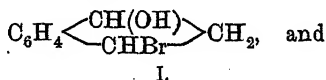
These results are somewhat higher than those obtained by Perkin and Révay, but, as will be seen from the following table, they are sufficiently close to show that the two synthetical preparations of indene are identical.

Synthetical indene (Kipping and Hall).....	$d_{40}^{40}$	1.0081
" " (Perkin and Révay) .....	"	1.0059
Coal-tar " (Krämer and Spilker) .....	"	1.0277
" " (examined by Perkin and Révay) .....	"	1.0600
" " ( " " " " ) .....	"	1.0479

Since the indene which we have obtained gives an oxybromide identical with that obtained from coal-tar indene, the two hydrocarbons must be identical, for if they had the different constitutions represented by the following formulæ,



they would give two isomeric dibromides, and the latter would yield two isomeric oxybromides, represented by the following formulæ :



Since, moreover, our hydrocarbon is identical with that of Perkin and Révay, it is proved that there is only one indene, the constitution of which is probably that of the unsaturated hydrocarbon shown above.

The expense incurred in carrying out this work was partly defrayed with the aid of a grant from the Government Grant Fund of the Royal Society, and the authors desire to record their thanks for the assistance thus afforded.

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## XLVII.—*Pilocarpine and the Alkaloids of Jaborandi Leaves.*

By HOOPER ALBERT DICKINSON JOWETT, D.Sc.

PILOCARPINE, the principal alkaloid contained in jaborandi leaves, was discovered by Hardy (*Bull. Soc. Chem.*, 1875, [ii], 24, 497) and by Gerrard (*Pharm. J.*, 1875, [iii], 5, 865, 965; 7, 225) independently in 1875, and crystalline salts were prepared by the latter chemist, but no detailed description of the salts was given nor were they analysed. In 1876, Kingzett (this Journ., 1876, ii, 30, 367) published an analysis of a platinichloride which had not been purified, and proposed the formula  $\text{C}_{23}\text{H}_{35}\text{O}_4\text{N}_4$ ; his results, however, agree within the limits of experimental error with the simpler formula,  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2$ . Harnack and Meyer (*Annalen*, 1880, 204, 67) later announced that

alkaloid was present in jaborandi leaves, and named it jaborine, its formula being given as  $C_{11}H_{16}O_2N_2$ . This base was amorphous and formed amorphous salts. These chemists also stated that pilocarpine on dry distillation with soda-lime yields trimethylamine. Methods of preparation of pilocarpine and a determination of its specific rotatory power were described by Petit (*Ber.*, 1877, 10, 896) and by Poehl (*Jahresb.*, 1880, 993, 1074). Chastaing (*Compt. rend.*, 1883, 97, 1435; 1885, 100, 1593) published a series of papers dealing with the chlorination and bromination of pilocarpine and its reaction with alkyl iodides. In 1885, Harnack and Meyer (*Chem. Centr.*, 1885, 628) described a third alkaloid in jaborandi leaves, which they named pilocarpidine and ascribed to it the formula  $C_{10}H_{14}O_2N_2$ . This base, although amorphous, gave a crystalline nitrate, melting at  $129.2^\circ$ , and no precipitate with auric chloride.

Between 1885 and 1887, Hardy and Calmels (*Compt. rend.*, 102, 1116, 1251, 1562; 103, 277; 105, 68) published a series of papers dealing with the description of various salts of pilocarpine and pilocarpidine, details of the conversion of the former into the latter, and experiments on the constitution of the alkaloid. They represented the base as a derivative of  $\beta$ -pyridinelactic acid and trimethylamine,

$C_5NH_4 \cdot C(CH_3) \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ N(CH_3)_3 \end{array} O$ , and claimed to have completed the proof of the constitution by a partial synthesis of the alkaloid. The account of their work, however, is very unsatisfactory and incomplete, and no reliance can be placed on their results: no description or analysis of the various crystalline salts is given and no proof is furnished of the identity of the product said to result from the decomposition of the alkaloid.

Nothing further was published till 1896, when Merck (*Merck's Ber.*, 1896, 11), and shortly afterwards Kundsén (*Ber. Pharm.*, 1896, 6, 164) reported their failure to confirm Hardy and Calmels' results. In this year also, Paul and Cownley (*Pharm. J.*, 1896, [iv], 3, 1, 437) drew attention to the unsatisfactory state of our knowledge of the subject, and noted the results of a few experiments on this group of alkaloids.

The first complete account of pilocarpine and its salts, as also of pilocarpidine, was given by Petit and Polonowsky (*J. Pharm.*, 1897, [vi], 5, 370, 430, 475; 6, 8). In addition to the physical constants and analyses of the salts, important observations were recorded as to the optical behaviour of the bases under varying conditions. These chemists were able to convert pilocarpine into pilocarpidine by heat or by the influence of alkali, proved that the latter was isomeric with the former, and asserted, although on very slender experimental evidence, the pilocarpidine so prepared was identical with that found in the also pointed out several inaccuracies in Hardy and

Calmels' work, particularly as regards the experiments on the synthesis of the base.

In 1898, Herzig and Meyer (*Monatsh.*, 19, 56) criticised Petit and Polonowsky's results, and stated that the relationship between pilocarpine and pilocarpidine was not so simple as was supposed. Merck (*Arch. Pharm.*, 1898, 236, 141) contended that the pilocarpidine of the latter chemists was simply altered pilocarpine, and showed that pilocarpidine (natural) underwent a similar change on heating. To these criticisms, Petit and Polonowsky replied that the pilocarpidine used by Merck was not a single substance, but was really impure pilocarpine.

It must be pointed out that a confusion of names has arisen, since Harnack and Merck use the name pilocarpidine for an alkaloid of formula  $C_{10}H_{14}O_2N_2$ , whilst Petit and Polonowsky apply it to a base isomeric with pilocarpine,  $C_{11}H_{16}O_2N_2$ , but as just stated do not establish conclusively its identity with the alkaloid accompanying pilocarpine in jaborandi leaves. Merck, in his last paper, relies entirely on his analytical results for the proof that no pilocarpidine is formed from pilocarpine, but if his formula is wrong and these bases are really isomeric, his experiments, instead of disproving Petit and Polonowsky's results, actually support them.

It will thus be seen from this brief summary of the work on pilocarpine that our knowledge of this group of alkaloids is unsatisfactory, and with the view of remedying these defects, the present investigation was undertaken.

The pilocarpine used in this investigation was obtained from the following sources: (i) as nitrate in unbroken packages from two manufacturers; (ii) prepared by myself from *Pilocarpus microphyllus* or Maranham jaborandi; (iii) from a very small sample of true jaborandi leaves, *P. jaborandi*, of which I have been unable to obtain further supplies. The purified alkaloids obtained from these sources proved to be identical.

It may be desirable to state here that throughout this investigation the greatest care has been taken to work with pure materials, and where the results differ from those of Petit and Polonowsky, the determinations have been repeated several times with different preparations. These authors give the melting points as uncorrected, and do not indicate that any special means were taken to ensure the purity of their products; such precautions are particularly necessary, owing to the ease with which pilocarpine is converted into isopilocarpine during the processes of regeneration, &c., and of conversion into different salts.

The results communicated in the present paper may be briefly summarised as follows:

1. The physical constants and descriptions of the salts of pilocarpine

as given by Petit and Polonowsky are generally confirmed with a few exceptions, the most important discrepancy being found in the melting point of the picrate.

2. The optical behaviour of pilocarpine has been thoroughly studied and some of Petit and Polonowsky's figures have been corrected, although their general conclusions are confirmed.

3. The acid character of pilocarpine has been investigated, and the previous work on this subject by Hardy and Calmels corrected.

4. The existence of a base isomeric with pilocarpine, produced from it by the action of heat or alkali, as previously stated, is confirmed. Since this base is isomeric with, and bears a close relation to pilocarpine, it is proposed to call it *isopilocarpine*. It is shown that the base can be distilled unchanged in a vacuum.

5. Some of the physical constants of isopilocarpine and its salts as given by Petit and Polonowsky for pilocarpidine are confirmed, and others corrected.

6. Proof is given of the existence of isopilocarpine in jaborandi leaves and in the pilocarpine nitrate of commerce.

7. The existence of the pilocarpidine of Harnack and Merck and their statements regarding its composition are confirmed; hence the use of the name pilocarpidine for isopilocarpine as suggested by Petit and Polonowsky must be abandoned. Some of the salts of this base are described.

8. The absence of pilocarpidine in the pilocarpine nitrate of commerce and in the varieties of jaborandi leaves at present on the market is proved.

9. The *jaborine* of Harnack is shown to be a mixture of pilocarpidine, isopilocarpine, and possibly a trace of pilocarpine, with colouring matter. No evidence has been obtained of the existence of an alkaloid with the properties of jaborine, or of other alkaloids than those described in this paper.

10. Several experiments on the constitution of pilocarpine have been repeated and the results of Hardy and Calmels corrected. Further experiments on this subject are in progress.

11. The physiological action of the pure salts and of some derivatives and other products obtained from jaborandi leaves is being investigated by Prof. C. R. Marshall, of University College, Dundee; a brief abstract of the results obtained is given in this paper.

## I. PILOCARPINE.

### *Salts of Pilocarpine.*

*Pilocarpine Nitrate*,  $C_{11}H_{16}O_2N_2 \cdot HNO_3$ , occurs in well-defined crystals and was recrystallised repeatedly from alcohol and from water



until the melting point and specific rotation were constant. It melts at  $178^{\circ}$  (corr.) and a determination of its specific rotation gave the following result :

$$\alpha_D = +15.87^{\circ}; l = 2 \text{ dcm.}; c = 9.572; [\alpha]_D = +82.90^{\circ}.$$

Determinations of the solubility of the salt in water and in absolute alcohol gave the following results :

(1.) In water: 6.89 of solution at  $20^{\circ}$  gave 0.925 salt; hence 1 part is soluble in 6.4 parts of water at  $20^{\circ}$ .

(2.) In absolute alcohol: 11.191 of solution at  $20^{\circ}$  gave 0.0414 salt; hence 1 part is soluble in 269.3 parts of absolute alcohol at  $20^{\circ}$ .

The dry salt was analysed with the following results :

0.1712 gave 0.305  $\text{CO}_2$  and 0.0994  $\text{H}_2\text{O}$ .  $\text{C} = 48.6$ ;  $\text{H} = 6.45$ .

$\text{NH}_3$  from 2 grams of salt neutralised 15.2 c.c. N acid.  $\text{N} = 10.6$ .

$\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2\cdot\text{HNO}_3$  requires  $\text{C} = 48.65$ ;  $\text{H} = 6.32$  per cent.

„ „ for N in base,  $\text{N} = 10.3$  „

*Pilocarpine Hydrochloride*, prepared by the usual methods, is easily obtained pure, and in very large crystals by crystallisation from strong alcohol. The pure salt melts at  $204\text{--}205^{\circ}$ , and a determination of its specific rotation gave the following result :

$$\alpha_D = +18.21^{\circ}; l = 2 \text{ dcm.}; c = 9.924; [\alpha]_D = +91.74^{\circ}.$$

On analysis, the following result was obtained :

1.0614 gave 0.6216  $\text{AgCl}$ .  $\text{Cl} = 14.48$ .

$\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2\cdot\text{HCl}$  requires  $\text{Cl} = 14.48$  per cent.

*Pilocarpine Hydrobromide* is obtained in beautiful crystals by the method employed for the hydrochloride. The pure salt melts at  $185^{\circ}$  (corr.), and a determination of its specific rotation gave the following result :

$$\alpha_D = +15.5^{\circ}; l = 2 \text{ dcm.}; c = 10.058; [\alpha]_D = +77.05^{\circ}.$$

These figures are higher than those given by Petit and Polonowsky, but the salt was recrystallised three times without alteration of the melting point; the lower figures previously given must have been those for an impure salt, due perhaps to a small quantity of isopilocarpine hydrobromide formed during the preparation.

On analysis, the following result was obtained :

0.5154 gave 0.3334  $\text{AgBr}$ .  $\text{Br} = 27.58$ .

$\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2\cdot\text{HBr}$  requires  $\text{Br} = 27.64$  per cent.

*Pilocarpine Sulphate* is somewhat difficult to obtain in crystals owing to its extreme solubility in water or absolute alcohol, but it can be obtained by adding anhydrous ether to a solution of the dried

salt in absolute alcohol and allowing to stand in a closed vessel. The pure salt melts at  $132^{\circ}$  (corr.) and a determination of its specific rotation gave the following result:

$$\alpha_D = +6.2^{\circ}; l = 1 \text{ dcm.}; c = 7.318; [\alpha]_D = +84.72^{\circ}.$$

*Pilocarpine Picrate* is obtained by adding a solution of picric acid to an aqueous solution of the hydrochloride, and can easily be crystallised from hot water or alcohol. It melts at  $147^{\circ}$  (corr.) and is particularly useful for identifying the base, even when mixed with isopilocarpine, as the picrates are somewhat easily separated by fractional crystallisation from water.

*Pilocarpine Aurichloride*,  $C_{11}H_{16}O_2N_2 \cdot HAuCl_4 \cdot H_2O$ .—Hardy and Calmels have described four compounds of gold chloride with pilocarpine, namely,  $B \cdot HAuCl_4$ ,  $B \cdot AuCl_3$ ,  $B(AuCl_3)_2$ ,  $B \cdot HAuCl_4 \cdot AuCl_3$ , and have specified the conditions under which they were formed, but give no analyses of the products. I have repeated their experiments, using excess of base, auric chloride, and hydrochloric acid respectively, and in every case obtained the normal aurichloride as the sole product.

On adding auric chloride to an aqueous solution of a salt of pilocarpine, a precipitate is obtained which quickly becomes crystalline. The air-dried salt melts indefinitely at about  $100^{\circ}$ . On analysis:

0.1764 gave 0.0612 Au. Au = 34.69.

$C_{11}H_{16}O_2N_2 \cdot HAuCl_4 \cdot H_2O$  requires Au = 34.82 per cent.

When the salt is dried for some time in a water-oven below  $100^{\circ}$ , it loses its water of crystallisation; the anhydrous compound melts indefinitely at  $117$ — $130^{\circ}$ . On analysis:

0.1496 gave 0.0538 Au. Au = 35.96.

$C_{11}H_{16}O_2N_2 \cdot HAuCl_4$  requires Au = 35.96 per cent.

The melting points of these salts are not at all sharp, and cannot be used for purposes of identification.

*Pilocarpine Gold Chloride*,  $C_{11}H_{16}O_2N_2 \cdot AuCl_3$ .—If the normal aurichloride is boiled with water or alcohol, it first dissolves, but crystals very quickly separate from the hot liquid, which is now strongly acid. These, when dry, melt sharply at  $163^{\circ}$  (corr.), thus differing considerably from the normal aurichloride. The dried salt was analysed with the following result:

0.09 gave 0.0344 Au. Au = 38.22.

$C_{11}H_{16}O_2N_2 \cdot AuCl_3$  requires Au = 38.51 per cent.

On adding a solution of auric chloride to the hydrobromide, a red precipitate was obtained, probably  $C_{11}H_{16}O_2N_2 \cdot HBr \cdot AuCl_3$ , but the substance was not further examined.

**Pilocarpine Platinichloride** is obtained by adding platinic chloride to a solution of pilocarpine hydrochloride; it forms silky plates, which can be recrystallised from hot acidified water. The recrystallised salt melts with decomposition at about  $218^{\circ}$  (corr.). On analysis:

0.0594 gave 0.0144 Pt. Pt = 24.24.

$(C_{11}H_{16}O_2N_2)_2, H_2PtCl_6$  requires Pt = 23.58 per cent.

No compound of the composition  $(C_{11}H_{16}O_2N_2)_2PtCl_4$ , as described by Hardy and Calmels, could be isolated.

**Pilocarpine Methiodide** is formed on dissolving dry pilocarpine in excess of methyl iodide, when the clear solution gradually deposits an oil, which, however, could not be crystallised.

**Pilocarpine Ethiodide** is obtained by dissolving pure dry pilocarpine in excess of ethyl iodide and allowing to stand, when an oil separates which slowly becomes crystalline. The compound may be recrystallised from alcohol and ether. It forms cubical crystals, very soluble in water or alcohol, and melts at  $114^{\circ}$  (corr.). On analysis:

0.3742 required 10.4 c.c.  $N/10$   $AgNO_3$  for precipitation. I = 35.25.

$C_{11}H_{16}O_2N_2, C_2H_5I$  requires I = 34.84 per cent.

A determination of the specific rotation gave the following result:

$\alpha_D = +2.71^{\circ}$ ;  $l = 1$  dm.;  $c = 4.158$ ;  $[\alpha]_D = +65.2^{\circ}$ .

#### *Properties of Pilocarpine.*

Pilocarpine is best obtained by adding excess of ammonia to an aqueous solution of one of its salts, and extracting two or three times with chloroform; after washing to remove ammonia, the chloroform solution, on evaporation or distillation, yields a colourless oil, which can be freed from the last traces of the solvent by leaving it in an open dish for several days. As thus obtained, pilocarpine is a thick oil, freely soluble in water, alcohol, or chloroform, but almost insoluble in ether or light petroleum. All efforts to crystallise it by ordinary methods failed. It can be distilled in a vacuum, but during this process undergoes change into isopilocarpine: thus, pure pilocarpine, after distillation at about  $260^{\circ}$  under 5 mm. pressure, was found to form a nitrate, which melted at  $146^{\circ}$ , this being the melting point of a mixture of pilocarpine and isopilocarpine, containing chiefly the latter.

Petit and Polonowsky state that pilocarpine and isopilocarpine are not extracted by chloroform from a solution of the salt rendered alkaline with caustic soda. The following experiment shows that it is possible

under those circumstances to extract an appreciable quantity of the bases.

Pilocarpine nitrate was dissolved in water, excess of soda added, and the liquid extracted four times with chloroform, 52.8 per cent. of the base being thus removed. The alkaline liquid was now rendered acid, excess of ammonia added, and the rest of the alkaloid extracted by shaking once with chloroform. Petit and Polonowsky's statement therefore requires modification. When the base is set free with caustic soda, it is extracted slowly and incompletely by chloroform; ammonia should, therefore, always be used.

### *Specific Rotation of Pilocarpine.*

Petit and Polonowsky found the specific rotation of the base to be  $+106^\circ$ , Poehl having previously obtained the value  $[\alpha]_D +101.6^\circ$ . But although aware of the fact that the base retains the last traces of solvent with great avidity, they do not indicate how this difficulty was overcome. In the following experiments, after the rotation had been taken, a known quantity of the liquid (for example, 4 or 5 c.c.) was placed in a tared dish, exactly neutralised with very dilute aqueous nitric acid, and evaporated to dryness in a vacuum desiccator. In this way, from the amount of nitrate found, the concentration of the solution used can be calculated. The following results were obtained:

$$\alpha_D = +10^\circ; l = 0.5 \text{ dm.}; c = 19.83; [\alpha]_D = +100.8^\circ$$

$$\alpha_D = +14.3^\circ; l = 1 \text{ dm.}; c = 14.188; [\alpha]_D = +100.8^\circ$$

$$\alpha_D = +2.1^\circ; l = 2.1 \text{ dm.}; c = 1.0641; [\alpha]_D = +100^\circ$$

$$\text{Mean of three determinations, } [\alpha]_D = +100.5^\circ$$

Petit and Polonowsky have shown that caustic alkali affects the rotation of pilocarpine in a peculiar manner, and explain this by supposing that the base is the anhydride of an acid with a lower rotation: on treatment with caustic soda, the salt is formed which gives the rotation of the acid. They boiled pilocarpine with excess of caustic soda, then titrated back with decinormal acid, so that there was exactly a molecule of caustic soda present to each molecule of pilocarpine, and, on examining the resulting solution, found that the specific rotation had fallen to  $+23.8^\circ$ . In the same paper, however, they point out that pilocarpine is converted into isopilocarpine by boiling with caustic soda, and as the latter has a lower rotation than the former, their experiment is invalid.

To ascertain the effect of alkali, mixtures of pilocarpine and caustic soda in varying proportions were made, one being kept for a month, whilst another was treated with hot caustic soda. The following results were obtained:

- (1.) 4 mols. of base to 1 mol. caustic soda.  
 $\alpha_D = +5.08^\circ$ ;  $l = 1$  dcm.;  $c = 5.949$ ;  $[\alpha]_D = +85.40^\circ$ .
- (2.) 2 mols. of base to 1 mol. caustic soda.  
 $\alpha_D = +3.716^\circ$ ;  $l = 1$  dcm.;  $c = 5.949$ ;  $[\alpha]_D = +62.47^\circ$ .
- (3.) 1 mol. of base to 1 mol. caustic soda.  
 $\alpha_D = +1.916^\circ$ ;  $l = 1$  dcm.;  $c = 5.949$ ;  $[\alpha]_D = +32.21^\circ$ .
- (4.) 1 mol. of base to 4 mols. caustic soda.  
 $\alpha_D = +1^\circ$ ;  $l = 1$  dcm.;  $c = 2.9745$ ;  $[\alpha]_D = +33.62^\circ$ .  
 This, after standing one month, gave  $[\alpha]_D = +31.5^\circ$ .  
 $\alpha_D = +0.6^\circ$ ;  $l = 1$  dcm.;  $c = 2.8376$ ;  $[\alpha]_D = +21.15^\circ$ .
- (5.) Boiled with excess of caustic soda for 10 minutes.

These experiments show that the specific rotation of pilocarpine with excess of the alkali is  $+31.5^\circ$ , and that the figure obtained by Petit and Polonowsky, namely,  $+23.8^\circ$ , is due to a slight decomposition into isopilocarpine. It was also found that this conversion of pilocarpine into the acid of lower specific rotation may take place, to a limited extent, in aqueous solution in the absence of alkali. Thus the specific rotation of pilocarpine in aqueous solution, after standing for 3 weeks, was:

$$\alpha_D = +5.5^\circ; l = 1 \text{ dcm.}; c = 7.094; [\alpha]_D = +77.53^\circ.$$

This solution gave a nitrate of melting point  $178^\circ$  (corr.), so that the base was pure pilocarpine.

An attempt was made to determine the rotation of free pilocarpic acid by preparing it from the barium salt, but low figures were obtained, which were found to be due to the partial conversion of pilocarpine into isopilocarpine by the alkali.

#### *Compounds of Pilocarpine with Metals.*

Hardy and Calmels stated that pilocarpine might be regarded as the anhydride of a hypothetical pilocarpic acid, and described the sodium, potassium, barium, copper, and silver salts. Petit and Polonowsky confirm this statement, describing, however, only the sodium and barium salts and the acid, which rapidly passed into the anhydride.

*Sodium Pilocarpate* is formed as a varnish by evaporating to dryness a solution of pilocarpine in water, to which a molecular proportion of soda has been added. As stated by Petit and Polonowsky, chloroform does not dissolve this salt or extract any alkaloid from it when dry; if, however, it is dissolved in water, an appreciable amount of the alkaloid can be removed by shaking with chloroform. The alkaloid can be titrated with alkali by boiling, and using phenolphthalein as an indicator; the end reaction, however, is not sharp.

The liquid remains colourless until about half the theoretical quantity of alkali has been added, and then gradually develops colour, but a decided red is not observed until practically the theoretical quantity of alkali has been added. This behaviour indicates the extraction of about 50 per cent. of the alkaloid from soda solution, as previously described.

*Barium Pilocarpate* can be obtained, as stated by earlier workers, by evaporating to dryness equivalent proportions of pilocarpine or the nitrate with baryta water, and extracting the residue with 90 per cent. alcohol. I attempted to prepare free pilocarpic acid from this salt by decomposing it with exactly the right amount of dilute sulphuric acid, and obtained a product having the following specific rotation:

$$\alpha_D = +1.5^\circ; l=1; c=8.73; [\alpha]_D = +17.18^\circ.$$

The melting point of the nitrate of this base was  $164^\circ$ , showing that the treatment with baryta converted some of the pilocarpine into isopilocarpine.

*Copper Pilocarpate*.—Hardy and Calmels stated that they prepared this salt by boiling a solution of barium pilocarpate to which a solution of a copper salt has been added, when it separated as a green powder, and they gave it the formula  $B_2Cu$ . I have obtained a similar result, but, on analysing the product, found it to be copper hydroxide:

0.1982 gave 0.1610 CuO. Cu = 64.90.

$B_2Cu$  requires Cu = 13.2;  $Cu(OH)_2$  requires Cu = 65.1 per cent.

Evidence, however, was obtained of the existence of copper pilocarpate, although the salt could not be isolated in a pure form.

When freshly precipitated copper hydroxide in excess is boiled with a solution of pilocarpine, part of it dissolves, and a dark blue solution is formed, which, when filtered and evaporated to dryness, gives a dark blue varnish. On analysis, the following result was obtained:

0.1912 gave 0.0136 CuO. Cu = 5.67 per cent.

A portion, well washed with chloroform to remove any free alkaloid, was also analysed:

0.1598 gave 0.019 CuO. Cu = 9.49.

$(C_{11}H_{15}O_3N_2)_2Cu$  requires Cu = 12.47 per cent.

The product was therefore copper pilocarpate, with a little pilocarpine adhering to it.

*Silver Pilocarpate*, as described by Hardy and Calmels, was silver oxide, but an impure salt may be obtained by treating pilocarpine with silver hydroxide, filtering, and evaporating the solution to dry-

ness. The product, however, as in the case of the copper salt, contained a large quantity of pilocarpine.

*Pilocarpine Argento-nitrate*,  $(C_{11}H_{16}O_2N_2)_2, AgNO_3$ .—Hardy and Calmels state that on mixing aqueous solutions of silver nitrate and pilocarpine, two crystalline substances are obtained, having either the formula  $B, AgNO_3$  or  $B, (AgNO_3)_2$ , according to whether excess of the base or silver salt is used. I have found that under both these conditions only one salt is formed, and analysis shows it to have a different composition from that previously assigned to it. The crystals melt at  $141^\circ$  (corr.) sharply, and the results of the analyses were as follows:

(1.) Salt prepared by adding excess of silver nitrate,

0.1578 gave 0.0254 Ag.  $Ag = 18.43$ .

(2.) Salt prepared by adding excess of pilocarpine,

0.1652 gave 0.0302 Ag.  $Ag = 18.28$ .

$(C_{11}H_{16}O_2N_2)_2, AgNO_3$  requires  $Ag = 18.41$  per cent.

These experiments are more in accord with the view that pilocarpine is a lactone and not a betaine as suggested by Hardy and Calmels.

## II. ISOPILOCARPINE.

### *Formation of Isopilocarpine from Pilocarpine.*

The formation of this base from pilocarpine by the action of heat or alkali was first noted by Petit and Polonowsky. Although its existence has been questioned by Merck, I am able to fully confirm Petit and Polonowsky's observation, but, as in the case of pilocarpine, some of the physical constants on record require modification. The name pilocarpidine, given to this base by Petit and Polonowsky is, however, inadmissible, since that name should be retained for a base,  $C_{10}H_{14}O_2N_2$ , found in jaborandi leaves, which has been partly described by Harnack and by Merck. As the new alkaloid is isomeric with pilocarpine and easily formed from it, I propose to term it *isopilocarpine*. This base, being so readily formed by the action of heat or alkali on pilocarpine, is very often present in it as an impurity, and many of the discrepancies between previous figures and my results are due to this fact. If pilocarpine hydrochloride is heated for half an hour at a few degrees above its melting point, or if some pure pilocarpine is distilled in a vacuum, a product is obtained which yields a crystalline nitrate melting at  $146^\circ$ , and this melting point is not affected by two or more recrystallisations of the salt. It is possible, however, to separate pilocarpine and isopilocarpine from the mixture. The base

is best obtained by heating an alcoholic solution of pilocarpine with alcoholic soda for some hours on a water-bath in a reflux apparatus, and on regenerating the base one or two crystallisations of the nitrate will yield a pure product melting at  $159^{\circ}$  (corr.). Most of the salts have been prepared from the base obtained both by the action of heat and of alkali on pilocarpine. The physical constants of these salts proved that the base formed by either method is isopilocarpine. These results necessitate a revision of the statement frequently met with, based on Hardy and Calmels' work, that "pilocarpidine, on heating, yields pilocarpidine, jaborine, and jaboric acid."

#### *Salts of Isopilocarpine.*

*Isopilocarpine Nitrate* can be obtained in very long prisms from water, or in short prisms from alcohol, and is insoluble in ether, chloroform, or acetone. It melts sharply at  $159^{\circ}$  (corr.), and one of many determinations of its specific rotation gave the following result:

$$\alpha_D = +4.7^{\circ}; l = 2 \text{ dm.}; c = 6.586; [\alpha]_D = +35.68^{\circ}.$$

The purity of the salt was determined by the fact that, after three recrystallisations from alcohol and from water, the melting point and specific rotation were unchanged. Determinations of the solubility in water and in absolute alcohol gave the following results:

(1.) In water: 4.402 solution at  $19^{\circ}$  gave 0.4696 salt; hence 1 part is soluble in 8.4 parts of water at  $19^{\circ}$ .

(2.) In absolute alcohol: 10.3924 solution at  $20^{\circ}$  gave 0.029 salt; hence 1 part is soluble in 357.3 parts of absolute alcohol at  $20^{\circ}$ .

Petit and Polonowsky give the solubility in 95 per cent. alcohol as 1 in 135, and of pilocarpine nitrate as 1 in 146. If this were so, the order of solubility of these salts in alcohol would be the reverse of that in water, which is improbable, and, as above shown, is not the case. On combustion, the dry salt afforded the following figures:

0.2578 gave 0.462  $\text{CO}_2$  and 0.1494  $\text{H}_2\text{O}$ .  $\text{C} = 48.87$ ;  $\text{H} = 6.43$ .

$\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2\cdot\text{HNO}_3$  requires  $\text{C} = 48.65$ ;  $\text{H} = 6.32$  per cent.

*Isopilocarpine Hydrochloride* can be obtained from the nitrate by the usual methods, and is best crystallised by adding ether to an alcoholic solution, as the salt is extremely soluble both in water and in absolute alcohol. The pure air-dried salt melts at  $127^{\circ}$  (corr.), and, unlike pilocarpine hydrochloride, is not hygroscopic, but stable in the air. It contains half a molecular proportion of water of crystallisation as shown by the following analysis:

0.3374, dried at  $110^{\circ}$  until constant, lost 0.012  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 3.5$ .

$(\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2\cdot\text{HCl})_2\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 3.55$  per cent.



A determination of its specific rotation gave the following result :

$$\alpha_D = +1.93^\circ; l=1 \text{ dm.}; c=4.974; [\alpha]_D = +38.8^\circ.$$

The anhydrous salt melts at  $159^\circ$  (corr.).

*Isopilcarpine Hydrobromide* is obtained in a similar manner to the hydrochloride by adding ether to an alcoholic solution. The crystals are anhydrous and melt at  $147^\circ$  (corr.). A determination of its specific rotation gave the following result :

$$\alpha_D = +1.5^\circ; l=2 \text{ dm.}; c=2.288; [\alpha]_D = +32.8^\circ.$$

*Isopilcarpine Picrate*, prepared by adding picric acid to the aqueous solution of the hydrochloride and recrystallising from water or alcohol, forms long, brilliant yellow needles which melt at  $161^\circ$  (corr.).

*Isopilcarpine Aurichloride* is formed by adding a solution of auric chloride to a solution of pure isopilcarpine hydrochloride, and allowing the amorphous precipitate to become crystalline. The crystals are anhydrous and melt at  $158-159^\circ$  (corr.). On analysis :

0.1888 gave 0.0678 Au. Au = 35.91.

$C_{11}H_{16}O_2N_2 \cdot HAuCl_4$  requires Au = 35.96 per cent.

*Isopilcarpine Gold Chloride* is prepared by boiling the aurichloride in water, when crystals separate exactly as in the case of the corresponding pilocarpine salt; these melt at  $185-186^\circ$  (corr.). On analysis :

0.1564 gave 0.0604 Au. Au = 38.61.

$C_{11}H_{16}O_2N_2 \cdot AuCl_3$  requires Au = 38.5 per cent.

*Isopilcarpine Platinichloride*, obtained by the usual method, crystallises in orange scales, which melt at  $226-227^\circ$  (corr.) with blackening and effervescence. On analysis :

0.2508 gave 0.0592 Pt. Pt = 23.60.

$(C_{11}H_{16}O_2N_2)_2 \cdot H_2PtCl_6$  requires Pt = 23.58 per cent.

*Isopilcarpine Methiodide* is obtained by dissolving pure dry isopilcarpine in excess of methyl iodide, allowing it to stand, then removing the excess of methyl iodide, and recrystallising the residue from absolute alcohol until pure. It melts at  $114^\circ$  (corr.). A determination of the specific rotation gave the following result :

$$\alpha_D = +0.83^\circ; l=1 \text{ dm.}; c=2.734; [\alpha]_D = +30.4^\circ.$$

On analysis, the following result was obtained :

0.2597 required 7.6 c.c. *N*/10 silver nitrate for precipitation. I = 37.1.

$C_{11}H_{16}O_2N_2 \cdot CH_3I$  requires I = 36.23 per cent.

*Properties of Isopilocarpine.*

Isopilocarpine can be obtained by a similar method to that used for pilocarpine, and the two bases possess very similar properties. Petit and Polonowsky have described it as forming large crystals, which are very hygroscopic, and soluble in all proportions in water and in alcohol. I have not obtained it in a crystalline form, but have found that it can be distilled in a vacuum without decomposition, and forms a colourless, viscid oil, becoming quite fluid on warming. It boils at  $261^{\circ}$  under 10 mm. pressure, and the distillate yields a nitrate melting at  $159^{\circ}$ , thus proving that the base distils unchanged. The specific rotation was observed with the same precautions as detailed under pilocarpine, with the following results :

$$\alpha_D = +5^{\circ}; l = 1 \text{ dcm.}; c = 11.652; [\alpha]_D = +42.91^{\circ}.$$

$$\alpha_D = +2.8^{\circ}; l = 1 \text{ dcm.}; c = 6.555; [\alpha]_D = +42.7^{\circ}.$$

$$\text{Mean of two determinations } [\alpha]_D = +42.8^{\circ}.$$

Three determinations of the specific rotation of the base, to which a molecular proportion of sodium hydroxide had been added, showed the solution to be inactive, and on adding excess of alkali no activity was observed.

*Copper Isopilocarpace* could not be obtained pure, though evidence of its existence was obtained. An aqueous solution of pure isopilocarpine was boiled with an excess of freshly precipitated copper hydroxide, filtered, and the blue filtrate evaporated to dryness; this was extracted with chloroform, the chloroform solution precipitated with ether, and the mother liquor evaporated to dryness. All three products were then analysed, with the following results :

(1). Portion insoluble in chloroform :

0.0744 gave 0.0068 CuO. Cu = 7.3 per cent.

(2). Portion soluble in chloroform, but precipitated by ether :

0.0888 gave 0.01 CuO. Cu = 8.99 per cent.

(3). Portion soluble in the mixture of chloroform and ether :

0.7238 gave 0.0192 CuO. Cu = 2.12 per cent.

$(C_{11}H_{15}O_3N_2)_2Cu$  requires Cu = 12.47 per cent.

The last product was chiefly isopilocarpine, but the others contained copper isopilocarpace.

*Isopilocarpine Argento-nitrate*.—On adding excess of silver nitrate in aqueous solution to an aqueous solution of isopilocarpine, an oily precipitate was obtained which contained silver, but could not be obtained crystalline.

*Existence of Isopilocarpine in the Alkaloids obtained from Jaborandi Leaves and in the Pilocarpine Nitrate of Commerce.*

The settlement of this question was one of the most important points in this inquiry, and unexpectedly proved to be a most difficult and tedious task. Harnack, and more recently Merck, have stated that the alkaloid yielding the crystalline nitrate accompanying pilocarpine is pilocarpidine,  $C_{10}H_{14}N_2O_2$ , and it has been generally assumed that any impurity in pilocarpine nitrate would be pilocarpidine nitrate, or less likely jaborine nitrate. Petit and Polonowsky, on the other hand, state that the impurity existing in the pilocarpine nitrate of commerce, sometimes to the extent of 50—60 per cent., is isopilocarpine nitrate, and that this alkaloid is found in the leaves. There are thus apparently two opposite statements, both supported by experimental proof. The only proof adduced by Petit and Polonowsky as to the identity of isopilocarpine prepared from pilocarpine with that obtained from the leaves, or from the pilocarpine nitrate of commerce, is that auric chloride behaves in precisely the same manner with isopilocarpine obtained from the first two sources.

My experiments prove conclusively that the impurity existing in the pilocarpine nitrate *at present* on the market, and in the alkaloid prepared from jaborandi leaves *at present* obtainable is isopilocarpine, identical with that formed from pilocarpine, and further that isopilocarpine exists ready formed in the leaves.

Two samples of pilocarpine nitrate from different manufacturers were used, and a quantity of impure pilocarpine nitrate was prepared from the jaborandi leaves at present in the market, called Maranham jaborandi. The process of purification employed was one of repeated fractional crystallisation until a product of constant melting point was obtained. All three products behaving similarly, they were at a certain stage mixed, and the results obtained therefore relate to all three specimens.

By repeated fractional recrystallisation, a nitrate was obtained of melting point  $146^\circ$ , which was not changed by two recrystallisations, and when obtained in two fractions both melted at  $146^\circ$ ; this was regarded as a pure product, and therefore was converted into the hydrochloride, from which, by recrystallisation from absolute alcohol, and finally by fractional recrystallisation from alcohol and ether, a quantity of pure pilocarpine salt was separated. A hydrochloride, however, was obtained melting at  $150^\circ$ , which was unchanged by two recrystallisations from alcohol and ether, and by collection in two fractions. From this product, the aurichloride, platinichloride, picrate, and base were prepared, and the hydrochloride, auri-

chloride, and platinichloride analysed. In all cases, melting points and specific rotations were obtained, differing but slightly from those of the corresponding isopilocarpine salts, and the analytical results agreed exactly with those required for the latter base. On recrystallisation of the hydrobromide and nitrate, however, the product was found to still contain pilocarpine; and from the nitrate—which was expected to melt at  $146^\circ$ , but which actually melted at  $150^\circ$ —by recrystallising it seven times, pure isopilocarpine was finally obtained. It had thus been necessary to recrystallise the nitrate and hydrochloride about 20 times and in about 40 fractions before obtaining a pure product and a satisfactory result.

The proof of the identity of the base with isopilocarpine was furnished by the physical constants and analyses of the base, nitrate, hydrochloride, hydrobromide, pierate, aurichloride, gold chloride, and platinichloride.

In view of the importance of this point, the analytical data are here given; the melting points in all cases agreed exactly with those recorded for the salts of isopilocarpine. The agreement of these figures likewise affords proof of the correctness of the constants previously given.

Base obtained from impure pilocarpine nitrate.

*Specific Rotation of Base:*

$$\alpha_D = +1.5^\circ; l = 1 \text{ dm.}; c = 3.549; [\alpha]_D = +42.2^\circ.$$

With excess of alkali,  $\alpha_D = 0^\circ$ .

*Nitrate.*—Specific rotation:

$$\alpha_D = +6.1^\circ; l = 2 \text{ dm.}; c = 8.784; [\alpha]_D = +34.72^\circ.$$

The solubility in water and in alcohol was determined, with the following results:

Solubility in water: 6.401 of solution at  $19^\circ$  gave 0.7262 salt; hence 1 part is soluble in 7.8 parts of water at  $19^\circ$ .

Solubility in absolute alcohol: 15.48 of solution at  $19^\circ$  gave 0.045 salt; hence 1 part is soluble in 343 parts of absolute alcohol at  $19^\circ$ .

*Hydrochloride.*—Specific rotation:

$$\alpha_D = +2.7^\circ; l = 1 \text{ dm.}; c = 7.036; [\alpha]_D = +38.3^\circ.$$

0.7278 lost 0.0242  $\text{H}_2\text{O}$  when the air-dried salt was dried until of constant weight.  $\text{H}_2\text{O} = 3.32$  per cent.

*Hydrobromide.*—Specific rotation:

$$\alpha_D = +0.75^\circ; l = 1 \text{ dm.}; c = 2.182; [\alpha]_D = +34.3^\circ.$$

*Aurichloride.*—Analysis: 0.1956 gave 0.0704 Au. Au = 35.99.

$\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2\text{HAuCl}_4$  requires Au = 35.96 per cent.

*Gold Chloride*.—Analysis: 0.0516 gave 0.0198 Au. Au = 38.37.

$C_{11}H_{16}N_2O_2 \cdot AuCl_3$  requires Au = 38.51 per cent.

*Platinichloride*.—Analysis: 0.12 salt gave 0.0282 Pt. Pt = 23.5.

$(C_{11}H_{16}O_2N_2)_2 \cdot H_2PtCl_6$  requires Pt = 23.58 per cent.

These figures, together with the melting points, afford conclusive proof of the identity of the base obtained from impure pilocarpine nitrate with isopilocarpine prepared from pilocarpine by the action of heat or alkali.

The mother liquors from the nitrate last obtained were then examined, and a base isolated which at first was thought to be a new alkaloid with a nitrate melting at 144°, as this constant was not altered by four recrystallisations. By preparing the picrate, however, and recrystallising several times, the base was found to be a mixture of pilocarpine and isopilocarpine.

In order to obtain further evidence that these mixtures, which in some respects behaved as a pure substance, consisted of pilocarpine and isopilocarpine, four mixtures of the nitrates were made in certain proportions and recrystallised from alcohol. The results fully confirmed those previously obtained.

(1) A mixture of 90 per cent. of pure pilocarpine nitrate and 10 per cent. of pure isopilocarpine nitrate, after one crystallisation, melted at 170°, and after five recrystallisations yielded pure pilocarpine nitrate.

(2) A mixture of equal parts of the two nitrates melted indefinitely at 144—147°, and after five recrystallisations yielded an impure product melting at 160—165°, which seemed to be unaltered by further recrystallisation.

(3) A mixture of 33 parts of pilocarpine nitrate and 66 parts of isopilocarpine nitrate melted at 144°, and this melting point was not altered by three recrystallisations.

(4) A mixture of 90 per cent. isopilocarpine nitrate and 10 per cent. pilocarpine nitrate melted first at 157°, and after two recrystallisations yielded pure isopilocarpine nitrate.

These experiments fully explain the difficulties above-mentioned, and also a statement that pure pilocarpine nitrate melting at 141.7° was not changed by recrystallisation (Paul and Cownley, *loc. cit.*). The alkaloid prepared by me from the leaves was not subjected to any conditions that would convert any appreciable amount of the pilocarpine into isopilocarpine; the latter, however, was found to be present, although only in small quantity, and it certainly exists in the leaves.

## III. PILOCARPIDINE.

Having failed to obtain pilocarpidine from either the pilocarpine nitrate of commerce or from the leaves, I procured a small quantity of the nitrate from Merck, and after verifying Merck's statements regarding its composition and properties, made another very careful search for the base both in pilocarpine nitrate of commerce and in *jaborandi* leaves, but with negative results.

*Salts and Properties of Pilocarpidine.*

*Pilocarpidine Nitrate*,  $C_{10}H_{14}O_2N_2 \cdot HNO_3$ , as obtained from Merck was in large, prismatic crystals which melted at  $135^\circ$  (corr.). It was purified by recrystallisation from absolute alcohol until of constant melting point, and then melted at  $137^\circ$  (corr.). The salt is anhydrous, and determinations of its specific rotation and solubility gave the following results:

$$\alpha_D = +5.2^\circ; l = 1 \text{ dcm.}; c = 7.104; [\alpha]_D = +73.2^\circ.$$

Solubility in water: 0.935 solution gave 0.3154 salt; hence 1 part is soluble in 2 parts of water at  $15^\circ$ .

Solubility in absolute alcohol: (i) 5.6152 solution gave 0.0672 salt; hence 1 part is soluble in 82.56 parts of absolute alcohol at  $15^\circ$ .

(ii) 6.0958 solution gave 0.0756; hence 1 part is soluble in 79.63 parts of absolute alcohol at  $15^\circ$ . Mean = 1 in 81.1.

It was noted that this nitrate was much more easily decomposed by heat than that of the other bases.

*Pilocarpidine Aurichloride*.—On adding auric chloride to a somewhat dilute solution of pilocarpidine nitrate, no precipitate was obtained, but crystals separated on spontaneous evaporation. These were recrystallised from glacial acetic acid, and melted at  $124\text{--}125^\circ$  (corr.).

*Pilocarpidine Platinichloride* was prepared in the usual way, and was obtained in yellow needles, which, when air-dried, melted at  $88\text{--}89^\circ$  (corr.), but when rendered anhydrous by heating at  $80^\circ$  for some time, then just above  $100^\circ$ , melted at  $187^\circ$  (corr.). The air-dried salt gave, on analysis, the following result:

0.1796, dried at  $80^\circ$  until constant, lost 0.1048  $H_2O$ .  $H_2O = 8.3$ .

0.1508 gave 0.0342 Pt. Pt = 22.67 per cent.

$(C_{10}H_{14}O_2N_2)_2 \cdot H_2PtCl_6 \cdot 4H_2O$  requires  $H_2O = 8.28$ ; Pt = 22.39 per cent.

The anhydrous salt was also analysed:

0.1648 gave 0.0402 Pt. Pt = 24.39.

$(C_{10}H_{14}O_2N_2)_2 \cdot H_2PtCl_6$  requires Pt = 24.41 per cent.

*Pilocarpidine Picrate* came down as an oil on attempting to crystallise from hot water the precipitate obtained by adding picric acid to the aqueous solution of the nitrate, and all attempts to crystallise it failed. This behaviour is very different from that of the picrates of pilocarpine and isopilocarpine, which crystallise with ease.

*Specific Rotation of the Base.*—An endeavour was made to determine this constant by a similar method to that employed for pilocarpine, but owing to the readiness with which pilocarpidine undergoes decomposition, a satisfactory result was not obtained. The nitrate was therefore dissolved in a little water, a molecular proportion of caustic soda added, the solution made up to a definite volume, and the rotation observed; then another molecular proportion of alkali was added, and the rotation again taken. The results were as follows:

$$\alpha_D = +1.25^\circ; l = 1 \text{ dm.}; c = 1.5374; [\alpha]_D = +81.3^\circ.$$

with alkali:

$$\alpha_D = +0.5^\circ; l = 1 \text{ dm.}; c = 1.419; [\alpha]_D = +35.2^\circ.$$

Pilocarpidine thus behaves similarly to the other bases examined.

*Non-existence of Pilocarpidine in Pilocarpine Nitrate of Commerce and in Jaborandi Leaves.*

The properties which differentiated pilocarpidine from the other bases were the great solubility of the nitrate in water or alcohol, and the formation of an amorphous picrate. The nitrate was repeatedly fractionated from absolute alcohol and from mother liquors, and the product having the lowest melting point was carefully examined for pilocarpidine by forming the platinichloride and the picrate.

From 28 grams of pilocarpine nitrate of commerce, a nitrate was obtained melting at  $143^\circ$ , and the mother liquors from this fraction gave a platinichloride melting at  $218^\circ$ , this being the melting point of pilocarpine platinichloride. The fraction melting at  $143^\circ$  crystallised in two fractions and gave melting points of  $150^\circ$  and  $143^\circ$  respectively. There was thus no evidence obtained of the existence of pilocarpidine in this sample of pilocarpine nitrate.

From the alkaloid obtained by working up a large quantity of the leaves, 90 grams of a nitrate melting from  $149$ — $160^\circ$  were obtained. This was converted into hydrochloride, recrystallised from absolute alcohol, and the alkaloid from the mother liquors converted into nitrate, which was treated as above described. The final fraction gave a nitrate melting at  $143^\circ$ , yielding an amorphous picrate, which afterwards, however, became mostly crystalline. The crystals proved to be chiefly pilocarpine picrate. The alkaloid was regenerated from the amorphous picrate and converted into the platinichloride, which

was amorphous, did not melt at  $250^{\circ}$  and was therefore not pilocarpidine. It was thus proved that the jaborandi leaves at present obtainable, consisting chiefly of *P. microphyllus*, contain no pilocarpidine.

#### IV. JABORINE.

This alkaloid has been described by Harnack and Meyer as existing in the mother liquors of pilocarpine, and as being an amorphous base yielding amorphous salts. It is stated to be less soluble in water, and more soluble in ether, than pilocarpine, and to be physiologically antagonistic to it, resembling atropine in its action. An attempt was made to isolate this alkaloid, if present, by its sparing solubility in water and its solubility in ether, since the other bases are not precipitated from their salts by ammonia, and are almost insoluble in ether. Indications of such an alkaloid had been obtained, as in some cases a precipitate was produced by ammonia. From the total alkaloid extracted by chloroform from a quantity of the leaves of *P. pennatifolius*, the only other variety obtainable besides *P. microphyllus*, resin was removed by dissolving it in alcohol and pouring into acidified water. The filtrate was then made alkaline with ammonia, the precipitate collected, redissolved in acidified water, and reprecipitated with ammonia, this operation being repeated several times, and the precipitate finally extracted with ether; a very small residue was obtained, which was not soluble in a little cold water, and did not seem to be basic. The yield of this substance was 2 per cent. of the total alkaloid, and it did not agree at all with the description given of jaborine.

A very large quantity of mother liquors from pilocarpine, prepared from *P. microphyllus*, treated in a similar manner, gave an ethereal extract which, when converted into a nitrate, yielded a crystalline salt melting at  $143^{\circ}$ , and consisted of pilocarpine and isopilocarpine, whilst the residue from the mother liquor gave only the faintest milkiess on adding ammonia.

The search for jaborine in these two varieties of leaves having thus proved to be abortive, a specimen of jaborine was obtained from Merck, and examined in the following manner. The product, which was a light brown oil smelling strongly of chloroform, was dissolved in a little absolute alcohol and poured into dilute acid, when a milkiess appeared and a slight scum separated. On adding ammonia, no precipitate was obtained; the liquid was therefore extracted three times with ether, and the ethereal extract, after washing with water, yielded on evaporation a very light coloured residue, amounting to 3 per cent. of the original substance. The aqueous liquid was further extracted with chloroform, which, on evaporation, left an



extract like the original substance. This amorphous residue was converted into nitrate, and by evaporation from alcoholic solution gave a crystalline product mixed with a little amorphous colouring matter. The crystals gave no precipitate with ammonia, melted at  $142^{\circ}$ , and on recrystallisation gave a salt melting at  $148^{\circ}$ . This formed a crystalline picrate from which, by recrystallisation, isopilocarpine picrate melting at  $161^{\circ}$  (corr.) was isolated.

The mother liquors from this salt gave an amorphous picrate, from which the base was regenerated and converted into nitrate, which contracted at  $137^{\circ}$  and melted at  $141^{\circ}$ . This alkaloid was therefore pilocarpidine, containing possibly a little pilocarpine.

It follows therefore that jaborine is not a homogeneous substance, but a mixture of isopilocarpine, pilocarpidine, and possibly pilocarpine, and, furthermore, that no alkaloid answering the description of jaborine can be found in the leaves.

It may be well at this point to offer what seems to be the correct explanation of the discrepancies existing between the statements of different chemists. When pilocarpine was first discovered, the source was *P. jaborandi*, containing pilocarpine, isopilocarpine, which was overlooked, and pilocarpidine. Within recent years, however, *P. jaborandi* has become scarce, and is not obtainable now in any quantity. It has been replaced by Maranham jaborandi from *P. microphyllus*, which contains no pilocarpidine. It has been assumed that the impurity accompanying pilocarpine nitrate was pilocarpidine nitrate, but in reality it was isopilocarpine nitrate. Petit and Polonowsky in their investigations discovered the isopilocarpine, but did not find pilocarpidine, and overlooked the possibility that pilocarpidine, as described by Harnack and by Merck, might exist, although not in the alkaloids they examined. Similarly, although Merck knew and was in possession of true pilocarpidine nitrate, he also overlooked the possibility of the existence of a third alkaloid, isopilocarpine, and described it as altered pilocarpine. All the experimental data support this explanation.

With regard to jaborine, although it is possible that such an alkaloid as described existed in *P. jaborandi*, it is certain that no such alkaloid exists in the jaborandi leaves at present obtainable, and that the jaborine of commerce is not a homogeneous substance, but a mixture of the three alkaloids with a little colouring matter. Furthermore, seeing that this alkaloid was described as amorphous, and no detailed examination made of it, it is possible that the alkaloid actually examined was an impure pilocarpine, and the balance of probability seems to be in favour of this explanation. Physiological experiments confirm the results of the chemical investigation with respect to the nature of jaborine.

## V. CONSTITUTION OF PILOCARPINE.

Allusion was made in the introduction to this paper to the structural formula proposed by Hardy and Calmels for pilocarpine and to the unsatisfactory character of the evidence on which it was based. I have repeated some of their experiments with quite different results, and therefore give the details of these and of some further preliminary work on this question. I wish, however, to reserve the subject of the constitution of the alkaloid for a future communication. Hardy and Calmels' formula is chiefly based on the supposed production of trimethylamine from pilocarpine by certain reactions; I have been unable to obtain any evidence of the formation of this base in any of my experiments. Leaving the question of the nature of the isomerism of pilocarpine and isopilocarpine to a later date, most of the present experiments have been made with carefully purified isopilocarpine nitrate, this being the more stable of the two isomerides.

*Action of Water and Alkali on Pilocarpine.*

It has been stated that pilocarpine, on boiling with water, yields methyl alcohol, trimethylamine, and  $\beta$ -pyridinelactic acid.

0.8 gram of pure pilocarpine was heated with water in a sealed tube at  $180^\circ$  for 4 hours. On opening the tube, and distilling, no trace of methyl alcohol or volatile alkali was found, whilst the residual liquid gave a quantitative yield of isopilocarpine nitrate, identified by its melting point, namely,  $159^\circ$ .

Treatment with 20 per cent. caustic potash solution in a similar manner gave an identical result.

The only product of this action is therefore isopilocarpine.

*Distillation of the Base with Soda-lime.*

Harnack and Meyer state that trimethylamine is formed in this reaction. One gram of pure pilocarpine nitrate was mixed with large excess of soda-lime, then strongly heated in a Jena glass tube, and the volatile products drawn by an aspirator through two wash bottles containing a known quantity of normal hydrochloric acid.

The acid was then titrated back with normal soda, and it was found that 6 c.c. of acid were neutralised, the theoretical amount required being 7.3 c.c. acid. The liquid was then made alkaline with caustic soda and distilled, when a distinct smell of ammonia and pyridine was noted. The distillate was acidified with hydrochloric acid, evaporated to dryness, and the resulting hydrochloride extracted with

absolute alcohol. Two portions were obtained, one of which was soluble, the other insoluble, in alcohol.

(1.) The substance insoluble in alcohol was ammonium chloride. The platinum salt was made and analysed.

0.27 gave 0.118 Pt.  $Pt = 43.7$ .

$(NH_3)_2H_2PtCl_6$  requires  $Pt = 43.91$  per cent.

(2.) The hydrochloride soluble in alcohol. On adding auric chloride to the aqueous solution, a yellow precipitate was obtained which quickly became crystalline, and when dried melted at  $185^\circ$  (corr.). The salt was analysed with the following result:

0.181 gave 0.0818 Au.  $Au = 45.2$ .

$C_6NH_6HAuCl_4$  requires  $Au = 45.64$  per cent.

The melting point of the aurichlorides of both 2- and 3-methylpyridine is about  $184^\circ$ , so the bases formed are ammonia and either 2- or 3-methylpyridine.

#### *Oxidation of Isopilocarpine with Permanganate.*

Hardy and Calmels state that pilocarpine, on oxidation with permanganate, yields ammonia, a little methylamine, and  $\beta$ -pyridine-tartronic acid, with traces of  $\beta$ -pyridinecarboxylic acid, which was precipitated with copper acetate. This experiment does not prove the presence of a trimethylamine group in the molecule.

4.5 grams of isopilocarpine nitrate, dissolved in a litre of water, were oxidised with 15.6 grams or 6 mols. of potassium permanganate dissolved in a litre of water, the whole warmed on a water-bath, and left overnight. The manganese dioxide was filtered off and washed thoroughly, the filtrate neutralised with hydrochloric acid, concentrated by evaporation, made alkaline with caustic soda, and distilled. The volatile bases were neutralised with hydrochloric acid, evaporated to dryness, and then separated by extraction with absolute alcohol. The larger portion was insoluble in alcohol, and proved to be ammonium chloride. The smaller portion was soluble in alcohol, and very hygroscopic; the platinichloride melted on heating, and, on analysis, proved to be the salt of methylamine.

0.077 gave 0.0324 Pt.  $Pt = 42$ .

$(CH_3 \cdot NH_2)_2H_2PtCl_6$  requires  $Pt = 41.3$  per cent.

The residue, after distillation, was neutralised with sulphuric acid, evaporated to dryness, and extracted with alcohol. The alcoholic extract gave no precipitate with copper acetate, auric chloride, or potassio-mercuric iodide. Two oils, however, have been separated

from it, one of which has the properties of a lactone. These products are being further investigated.

*Action of Fused Caustic Potash on Isopilocarpine.*

1 gram of pilocarpine nitrate was mixed with a little aqueous potash and gradually added to 10 grams of fused caustic potash in a Jena glass tube, arranged as described in the experiment of distillation with soda-lime. The fused mass was very slightly discoloured. The volatile products, on titration, required 4 c.c. of normal hydrochloric acid. This is almost the theoretical quantity for half the nitrogen contained in pilocarpine. The hydrochloride was evaporated to dryness and heated with absolute alcohol, in which part dissolved and part was insoluble.

The portion insoluble in absolute alcohol was ammonium chloride. The platinichloride was analysed with the following result:

0.073 gave 0.0322 Pt.  $Pt = 44.1$ .

$(NH_3)_2H_2PtCl_6$  requires  $Pt = 43.9$  per cent.

The portion soluble in absolute alcohol was hygroscopic, and proved to be methylamine hydrochloride; it gave a fusible platinichloride, which was analysed with the following result:

0.0368 gave 0.0154 Pt.  $Pt = 41.8$ .

$(CH_3 \cdot NH_2)_2H_2PtCl_6$  requires  $Pt = 41.3$  per cent.

The fused mass was now acidified with dilute sulphuric acid and distilled, when a product smelling strongly of isobutyric acid, with a trace of acetic acid, was obtained. The distillate was digested with freshly precipitated silver hydroxide, filtered, and the filtrate concentrated, when crystals were obtained which were slightly reduced. On analysis:

0.1482 gave 0.0852 Ag.  $Ag = 57.4$  per cent.

The residue, after distillation, was extracted with ether; the ethereal extract, on evaporation, yielded an acid having the unmistakable odour of isobutyric acid. The silver salt of this product was analysed with the following result:

0.017 gave 0.0098 Ag.  $Ag = 57.6$ .

$C_4H_9O_2Ag$  requires  $Ag = 55.4$  per cent.

Although the results of these analyses are high for isobutyric acid, yet this is probably present, with perhaps a trace of acetic acid, which would slightly raise the percentage of silver. The reaction is being further investigated.

*Action of Caustic Potash on Pilocarpine and Isopilocarpine Methiodides.*

About 2 grams of the methiodide were dissolved in 20 per cent. aqueous caustic potash, and heated in a sealed tube at  $180^{\circ}$  for 4 hours. The product was then distilled, the volatile bases collected, and the amount determined by titration with normal hydrochloric acid. The hydrochlorides were obtained by evaporation of the aqueous solution and examined. The liquid was now acidified with sulphuric acid and distilled, the distillate examined for volatile acids, and the acid liquid then extracted with ether for acids soluble in this medium. The liquid was afterwards made alkaline with ammonia, and extracted with chloroform for fixed bases. The residue was neutralised and evaporated to dryness, as it was intended to extract it with alcohol to see if any other product was formed, but the iodides present interfered with the operation, and it was abandoned.

The following results were obtained:

(1.) With pilocarpine.

Volatile bases. The hydrochloride was entirely soluble in absolute alcohol and was obtained in three fractions, each fraction being converted into the platinichloride and analysed, giving Pt = 41.1, 41.1, and 41.0 per cent. respectively. The base was homogeneous and was methylamine. No acid or other product was obtained and the final residue gave no precipitate with copper acetate.

(2.) With isopilocarpine.

Volatile bases. The hydrochloride was entirely soluble in absolute alcohol and the platinichloride obtained in three fractions was analysed, giving Pt = 41.2, 41.2, and 41.4 per cent. respectively, thus proving the base to be methylamine.

A trace of hydrocyanic acid was found, but no other product and no substance giving a precipitate with copper acetate could be isolated. The pyridinecarboxylic acids give a precipitate with copper acetate, and this reagent is generally used for separating and identifying them.

Acetyl chloride has no action on these alkaloids, and they are remarkably stable towards nitric acid. Cold fuming nitric acid has no action on either base, but on warming, pilocarpine is converted into isopilocarpine, which is not attacked even by warm fuming nitric acid unless the action be prolonged.

Preliminary physiological experiments on isopilocarpine, pilocarpine, and pilocarpidine have been made by Prof. Marshall, of University College, Dundee, who reports that the substances produce similar

effects on the secretory activity of the sweat and salivary glands, pilocarpine being much the most powerful. Isopilocarpine is comparatively less depressant to the hearts of rabbits, but not to those of cats or man. The jaborine of Merck possesses a mild pilocarpine effect.

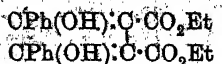
Having finished the characterisation of this group of alkaloids and repeated the work previously done on the subject, I am now engaged on experiments dealing with the constitution of pilocarpine, and hope soon to be in a position to communicate the results to the Society.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES.

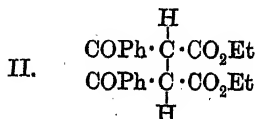
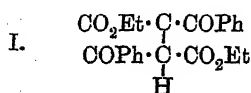
### XLVIII.—*Spectrographic Studies in Tautomerism. The Absorption Curves of the Ethyl Esters of Dibenzoylsuccinic Acid.*

By WALTER NOEL HARTLEY, F.R.S., and JAMES J. DOBBIE, M.A., D.Sc.

ACCORDING to theory, thirteen isomerides of diethyl dibenzoylsuccinate have a possible existence, but only three have so far been prepared and studied. On chemical grounds, Knorr (*Annalen*, 1896, 293, 70) regards one of the three as an enolic, and the other two as ketonic esters. He assigns to the enolic or  $\alpha$ -ester the constitutional formula,



without deciding which of the three possible stereo-isomeric modifications of this formula represents the substance examined by him. The two ketonic esters have the same constitutional but different stereo-isomeric formulæ. To one of them, which he designates the para- or  $\beta$ -ester, Knorr assigns the formula I, and to the other, which he designates the meso-, anti-, or  $\gamma$ -ester, the formula II.



A mixture of the  $\beta$ - and  $\gamma$ -esters is readily obtained by adding an ethereal solution of iodine to the sodium derivative of ethyl benzoylacetate, obtained by the action of metallic sodium on an ethereal solution of the ester. The two ketonic esters are readily separated

from one another by fractional crystallisation. When either of them is treated with sodium methoxide, a yellow, crystalline meal, consisting of the sodium derivative of the  $\alpha$ -ester, is obtained. The aqueous solution of this substance, when treated with excess of dilute sulphuric acid at the freezing temperature, yields the  $\alpha$ -ester, which separates as a thick oil possessing the colour of chlorine gas. The  $\beta$ -ester, which was first described by von Baeyer and Perkin (*Ber.*, 1884, 17, 60), melts at 128—130°, the  $\gamma$ -ester at 75°, and the former is less soluble than the latter in most solvents. Both esters are optically active. The ketonic esters are neutral to litmus, and practically insoluble in cold dilute alkalis. In their chemical properties, they are exactly alike.

The  $\alpha$ -ester differs, both in physical and chemical properties, from the ketonic esters. It is an oily liquid, has a strongly acid reaction, and dissolves in cold dilute alkalis. It gives a characteristic dirty brown coloration with ferric chloride, which is not shown by the ketonic esters, and moreover is unstable, gradually passing into a mixture of the  $\beta$ - and  $\gamma$ -esters at the ordinary temperature, the change taking place quickly at 130°.

If the view put forward by Knorr as to the relation of the three esters to one another is correct, the  $\beta$ - and  $\gamma$ -esters should give very similar, if not identical, absorption curves, since stereo-isomerides with right- and left-handed rotation, so far as they have been investigated in essential oils and their hydrocarbons, are not found to differ either in the amount or the character of their absorption. The  $\alpha$ -ester, on the other hand, having a different constitution, should exhibit a distinct series of absorption spectra.

We have photographed and measured the spectra of alcoholic solutions of the three substances, and the results obtained entirely bear out the conclusions arrived at by Knorr on purely chemical grounds. The spectra of the ketonic esters are identical. The amount of absorption is considerable, all rays beyond  $1/\lambda$  2795 being cut off by a layer 25 mm. thick of a solution containing 1 milligram-mol. in 100 c.c. of alcohol. There is also a well marked band of selective absorption reaching from  $1/\lambda$  3824 to  $1/\lambda$  4306 in a layer 3 mm. thick of a solution containing 1 milligram-mol. of the ester in 2500 c.c. of alcohol. This band is very persistent, and is still distinctly marked in a layer 4 mm. thick of a solution containing only 1 milligram-mol. in 12,500 c.c. of alcohol.

The spectrum of the  $\alpha$ - or enolic form is quite different from that of the ketonic esters. The general absorption is greater, a layer 25 mm. thick of a solution containing 1 milligram-mol. in 100 c.c. of alcohol cutting off all rays beyond  $1/\lambda$  2171. The absorption band of the

ketonic esters is altogether absent, whilst a well marked band makes its appearance in a layer 5 mm. thick of a solution containing 1 milligram-mol. in 500 c.c. of alcohol between  $1/\lambda$  2546 and  $1/\lambda$  3148. This band quickly dies out, no trace of it being visible in a layer 4 mm. thick of a solution containing 1 milligram-mol. in 500 c.c. of alcohol.

The absorption curves for the ketonic and enolic forms are shown in the diagram on p. 501.

When the solution of the  $\alpha$ -ester was allowed to stand and photographs were taken after successive intervals of time, the transition from the enolic to the ketonic form could be clearly traced. *After an interval of only three hours, the absorption band of the enolic ester had almost entirely disappeared whilst the amount of general absorption had also appreciably diminished.* Solutions containing one milligram-mol. in 100 and 500 c.c. respectively showed after 48 hours a great diminution in the amount of the general absorption, whilst after three weeks the curve coincided almost exactly with that of the  $\beta$ - and  $\gamma$ -esters, as shown on p. 502.

The result of this investigation exemplifies the value of the spectrographic method and shows how it might be applied with advantage to the investigation of similar cases of isomerism either to guide the chemical investigation or to confirm the conclusions drawn from it, especially when any doubt exists as to whether the isomerism is due to a difference in constitution or merely to a difference in the arrangement of the atoms in space. The amount of substance required for the experiments is small and can generally be recovered again from the solution.

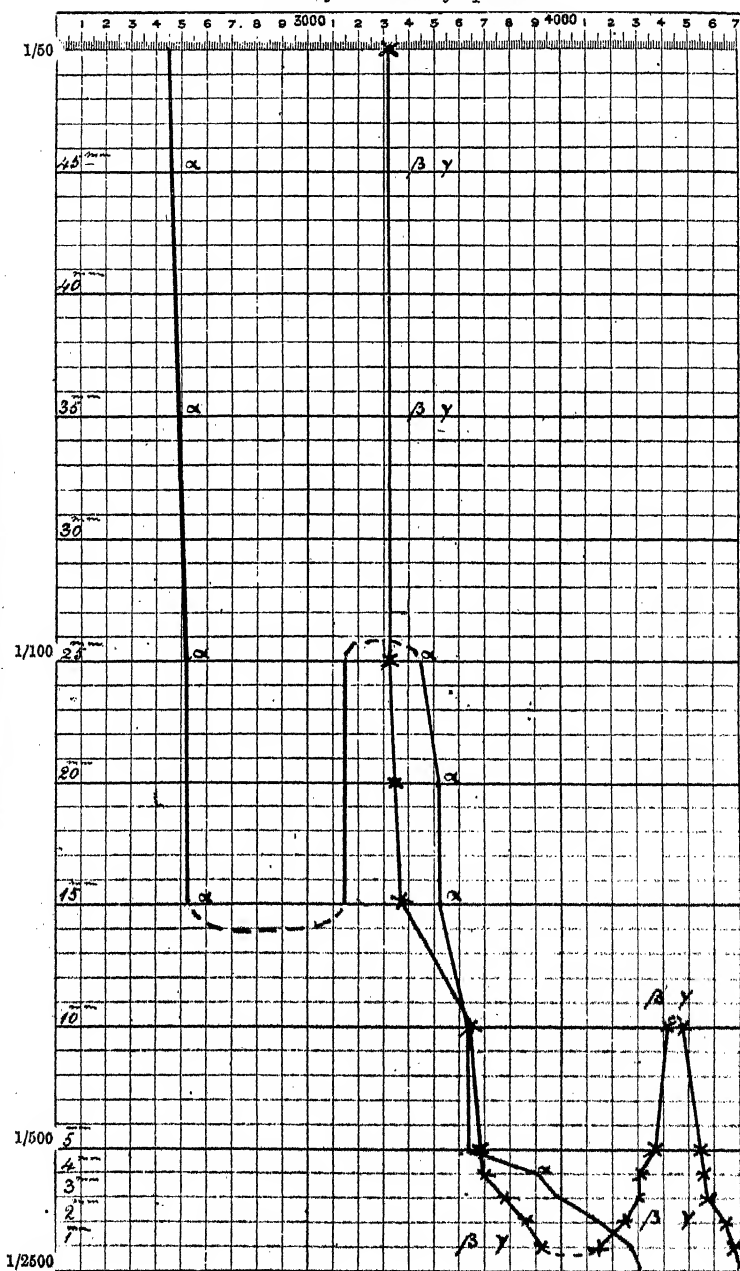
The esters were prepared by the method described by Knorr (*loc. cit.*). The preparation of the  $\beta$ - and  $\gamma$ -esters offers no difficulty, the  $\alpha$ -ester is only obtained when strict attention is paid to all the details given by Knorr. Two distinct preparations of each of the ketonic esters and three preparations of the  $\alpha$ -ester were made. Each preparation was photographed several times without any difference being observed in the photographs of the same substance. In the case of the  $\alpha$ -ester, the photographs were taken immediately after the completion of the preparation, as the change to the ketonic form sets in almost at once.

The reader is referred to the paper on "the absorption spectra of isatin, carbostyryl and their alkyl derivatives in relation to tautomerism" (Trans., 1899, '75, 649), and to publications therein mentioned for an account of the method used in drawing the accompanying curves.

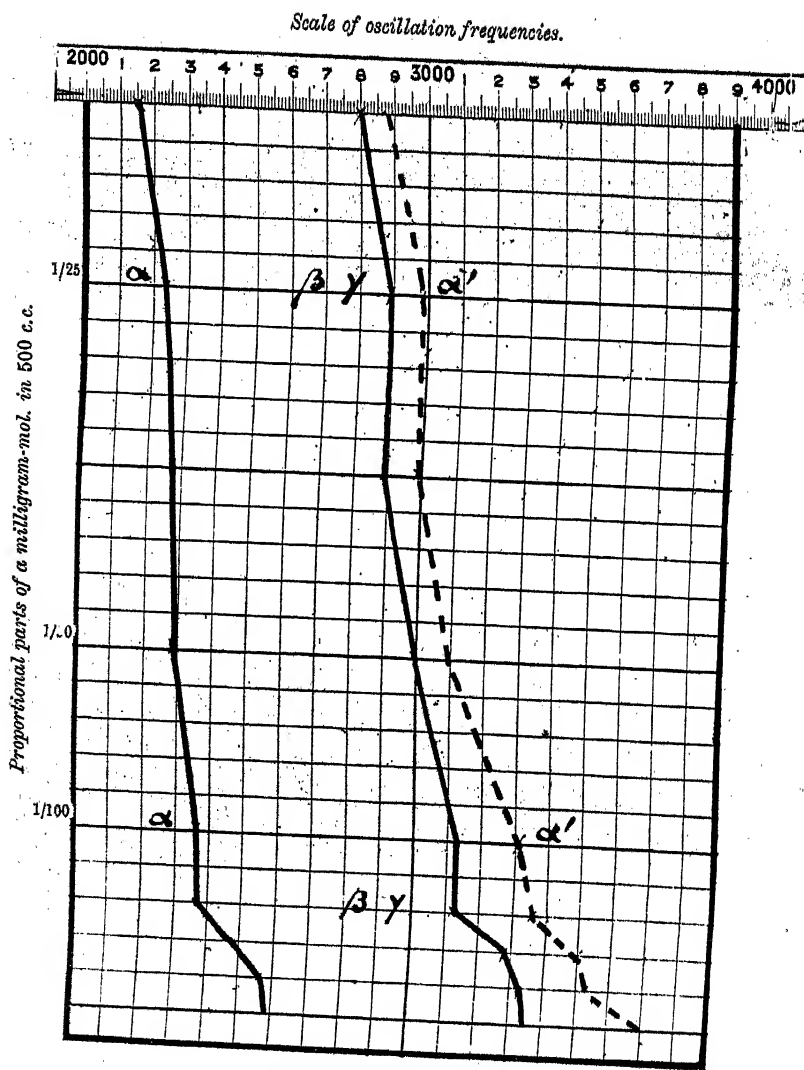


Scale of oscillation frequencies.

the  
Proportional parts of a milligram-mol. in 2500 c.c.  
The curves for the  $\beta$ - and  $\gamma$ -esters are identical, and are indicated by stars upon the line at points where measurements  
spectra were made. The curve of the  $\alpha$ -ester is indicated by  $\alpha$ .



Curves of molecular vibrations.



*Curves of molecular vibrations.*

*Ethyl  $\alpha$ -,  $\beta$ -, and  $\gamma$ -dibenzoylsuccinates.  $\alpha$  and  $\alpha'$  are the curves of the  $\alpha$ -ester, the former when the substance was freshly prepared, the latter when it had been kept for three weeks. The curves of the  $\beta$ - and  $\gamma$ -esters are identical, and are shown as one,  $\beta$ ,  $\gamma$ .*

## MEASUREMENTS.

*Ethyl  $\beta$ - and  $\gamma$ -Dibenzoylsuccinate,  $C_{22}H_{22}O_6$ .*

The two series of photographs from the  $\beta$ - and  $\gamma$ -esters are identical, therefore only one series of numbers is given.

0.382 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to..... Very faint continuation of spectrum to 2884. Complete absorption beyond.	2795	3577
20	Spectrum continuous to..... Complete absorption beyond.	2884	3467
15	The same.		
10	Spectrum continuous to..... Faint continuation of spectrum from 2884— 2892. Complete absorption beyond.	2884	3467
5	Spectrum continuous to..... Complete absorption beyond.	3148	3176
4	Spectrum continuous to..... Line showing very faintly at 3188.	3148	3176
3	Spectrum continuous to..... Complete absorption beyond except lines at 3188 and 3295.	3148	3176
2	Spectrum continuous to..... Line at 3323 very faint. Complete absorption beyond.	3295	3034
1	Spectrum continuous to..... Faint line at 3355. Complete absorption beyond.	3323	3009

0.382 gram in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to..... Complete absorption beyond.	3355	2980
3	Spectrum continuous to..... Very faint prolongation to..... Complete absorption beyond.	3355 3638	2980 2748
2	Spectrum continuous to..... Faint line at 3694. Lines at 4413, 4538, and 4555.	3638	2748
1	Spectrum continuous to..... Faint line at 4368. Lines at 4413, 4538, and 4555.	3694	2707

0.382 gram in 2500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to ..... Feeble transmission of strong lines 3754 to 4580.	3894	2707
3	Spectrum continuous to ..... A line faintly visible at 3824. <b>Absorption band</b> .....	3754	2869
	Lines transmitted $1/\lambda$ 4306 to 4555.	3824 to 4306	2615 to 2322
2	Spectrum continuous to ..... <b>Absorption band</b> .....	3824	2615
	Complete transmission to .....	3824 to 4246	2615 to 2355
1	Spectrum continuous to ..... <b>Absorption band</b> .....	4656	2147
	Spectrum beyond transmitted (faintly 4119 to 4246) to .....	3886	2573
		3886 to 4119	2573 to 2437
		4656	2147

0.382 gram in 12,500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
mm.			
4	Spectrum continuous to ..... <b>Absorption band</b> .....	3886	2573
	Spectrum continuous to .....	3886 to 4112	2573 to 2427
3	Spectrum weak between $1/\lambda$ 3886 and 4112, otherwise transmitted.	4656	
2	Spectrum continuous.		

*Ethyl α-dibenzoylsuccinate, C<sub>22</sub>H<sub>22</sub>O<sub>6</sub>.*

(1) Photographed immediately on completion of preparation.

0.382 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to..... Complete absorption beyond.	2171	4606
20	Spectrum continuous to..... Complete absorption beyond.	2246	4452
15	Blank (photograph failed).		
10	Spectrum continuous to..... Complete absorption beyond.	2278	4389
5	Spectrum continuous to.....	2354	4248
4	The same, but somewhat stronger.		
3	Spectrum continuous to..... Faint line at 2462.	2354	4248
2	Spectrum continuous to..... Very faint line at 2558. Complete absorption beyond.	2462	4061
1	Spectrum continuous to..... <b>Absorption band.....</b> Faint indications of lines from 2613 to Weak continuous spectrum from 3148 to Complete absorption beyond.	2546 <b>2546 to 3148</b> 2938 3478	3927 <b>3927 to 3176</b> 3403 2875

0.382 gram in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to..... Lines similar to preceding, but more strongly marked, additional line also at 3521.	2546	3927
3	The same.		
2	Spectrum continuous to..... Lines at 3694 and 3824. Complete absorption beyond.	3638	2748
1	Spectrum continuous to..... Lines at 3694, 3754, 3824, 3886.	3638	2748

0.382 gram in 2500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum nearly continuous to..... Faint line at 3897.	3886	2573
3	Very faint lines at 4002, 4038, 4115, 4129. Spectrum continuous to..... Very faint prolongation to .....	3897- 3963	2566 2523
2	Other lines as in preceding. Spectrum practically continuous to..... Still weak between 3886 and 4128.	4137	2417
1	Complete absorption beyond. Spectrum practically complete to..... Faint lines beyond at 4306, 4321, 4368, 4414, 4540, 4555.	4176	2394

(2) Photographed 3 hours after completion of preparation.

0.382 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to .....	2278	4889
20	Complete absorption beyond. Same as above.		
15	Spectrum continuous to .....	2296	4855
10	Complete absorption beyond. Spectrum continuous to .....	2354	4248
5	Complete absorption beyond. Spectrum continuous to .....	2463	4060
4	Complete absorption beyond. Spectrum continuous to .....	2503	3995
3	The same, but stronger.		
2	Spectrum continuous to .....	2547	3926
	<b>Absorption band.</b> ..... With lines showing faintly at 2719, 2750, 2768, and 3345. Spectrum nearly complete from 2983 to 3323.	2547 to 2983	3926 to 3352
1	Spectrum nearly continuous to .....	3355	2980
	Still weak in position of absorption band of $\alpha$ -ester.		

0.382 gram in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to.....	3521	2840
3	The same, with lines at 3563 and 3633.		
2	Spectrum continuous to.....	3633	2752
	Very faint lines at 3748, 3820, and 3885.		
1	Spectrum continuous to .....	3885	2594
	but weak beyond 3633		

(3) Photographed 24 hours after preparation.

0.382 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$ .	$\lambda$ .
25	Spectrum continuous to.....	2530	3952
	Very faint prolongation to.....	2673	3741
20	Spectrum continuous to.....	2768	3612
	Lines at 2790 and 2884.		
15	The same.		
10	Spectrum continuous to.....	2938	3403
	Lines showing faintly at 2982, 3000, 3042, 3064. Complete absorption beyond.		
5	Spectrum continuous to.....	3183	3141
4	The same, with line at 3295.		
3	Spectrum continuous to.....	3323	3009
2	" " .....	3355	2980
1	" " .....	3486	2868
	Line at 3521.		

0.382 gram in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$\frac{1}{\lambda}$ .	$\lambda$ .
4	Spectrum continuous to.....	3521	2840
3	" " ..... Line at 3638.	3563	2806
2	The same, with lines at 3707, 3748, and 3824.		
1	Spectrum continuous to ..... With lines at 3675, 3748, 3824, 3885.	3638	2748

(4) Photographed 48 hours after preparation.

0.382 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to.....	2501	3998
20	" " .....	2796	3576
15	The same.		
10	Spectrum continuous to.....	3064	3263
5	" " .....	3179	3145
4	" " .....	3310	3021
3	" " .....	3323	3009
2	" " .....	3355	2980
1	" " .....	3390	2949

0.382 gram in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to.....	3521	2840
3	" " .....	3638	2748
2	" " .....	3688	2748

(5) Photographed 3 weeks after preparation.

0.382 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to.....	2884	3467
	Lines beyond to 2982.		
20	Spectrum continuous to.....	3064	3263
15	The same.		
10	Spectrum continuous to .....	3148	3176
5	" " .....	3179	3145
4	" " .....	3179	3145
	Faint prolongation to 3323.		
3	Spectrum continuous to.....	3323	3009
2	" " .....	3355	2980
1	" " .....	3355	2980
	Faint prolongation to 3455.		



0.382 gram in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to.....	3521	2840
3	The same.		
2	Spectrum continuous to.....	3638	2748
1	" " .....	3886	2573

Our best thanks are due to Prof. Knorr for kindly assisting us in overcoming certain difficulties which we met with in the preparation of the  $\alpha$ -ester and to Mr. R. D. Abell, B.Sc., 1851 Exhibition Scholar, of the University College of North Wales, Bangor, for assistance in the general work of the research.

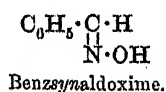
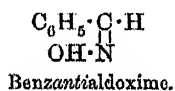
The expenses connected with the preparation of the substances required for this investigation were defrayed by a grant from the Government Research Fund of the Royal Society.

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DUBLIN.

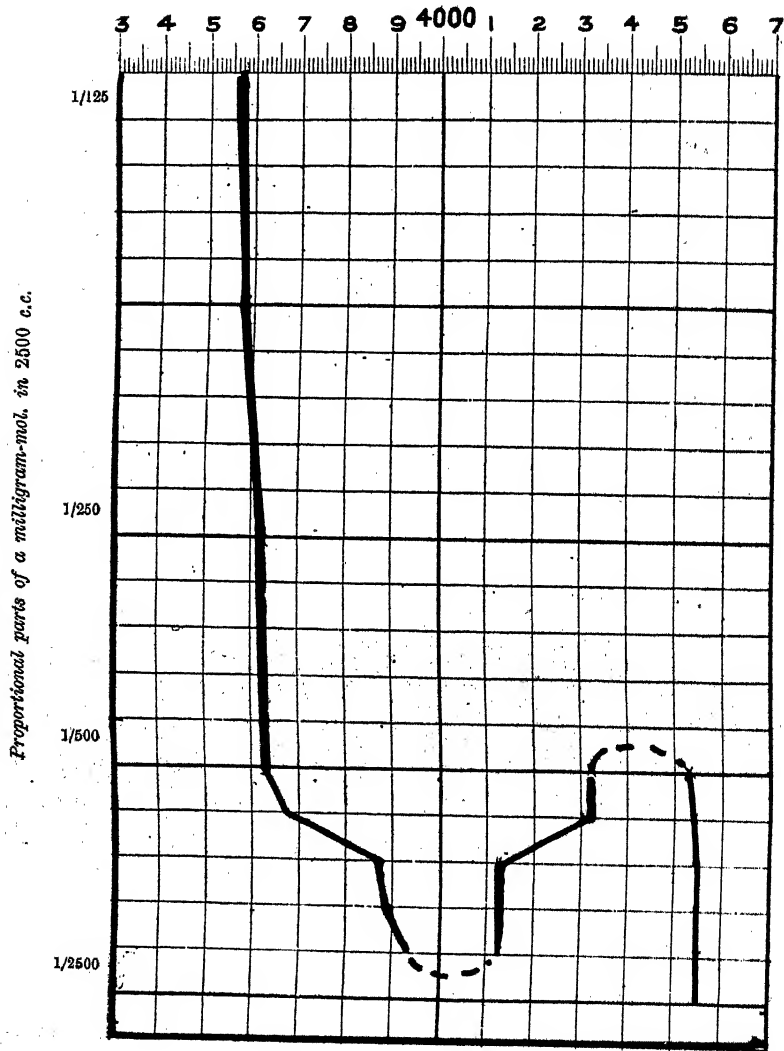
### XLIX.—*The Curves of the Molecular Vibrations of Benzantialdoxime and Benzsynaldoxime.*

By WALTER NOEL HARTLEY, F.R.S., and JAMES J. DOBBIE, D.Sc., M.A.

Benzantialdoxime and benzsynaldoxime are now generally represented by the following formulæ:



If these formulæ correctly represent the constitution of the two forms of benzaldoxime and their relation to one another, we should expect both compounds, as stereo-isomerides, to exhibit the same character and amount of absorption. As a matter of fact, we have found that the curves of the molecular vibrations of the two substances in ethereal solution are identical. A layer 25 mm. thick of a solution of either form of the aldoxime containing 1 milligram-mol. dissolved in 100 c.c. of absolute ether, absorbs all rays to  $1/\lambda$  3323 ( $\lambda$  3009). A

*Oscillation frequencies.**Curve of molecular vibrations.**Benzantialdoxime.**Benzsynaldoxime.*

layer 1 mm. thick of a solution containing 1 milligram-mol. in 500 c.c. of ether transmits all rays to  $1/\lambda$  3638 ( $\lambda$  2748), and shows an absorption band reaching from  $1/\lambda$  3638 ( $\lambda$  2748) to  $1/\lambda$  4321 ( $\lambda$  2314). This band is still distinctly traceable in a layer 1 mm. thick of a solution containing 1 milligram-mol. in 2500 c.c. of ether.

The benzaldoximes used in the experiments were prepared by the method given by Beckmann (*Ber.*, 1890, 23, 1684). The benzantialdoxime at 10 and 14 mm. pressure respectively was found to have the boiling point given by Luxmoore (*Trans.*, 1896, 69, 177) for those pressures. The benzsynaldoxime was photographed immediately after preparation. It was afterwards recovered from the ethereal solution and the melting point redetermined, when it was found that no decomposition had occurred while the photographs were being taken.

These results, which are shown in the curve on p. 510, confirm the conclusion previously arrived at, that stereo-isomerides, unlike isomerides which differ in structure, give identical absorption spectra.

#### MEASUREMENTS.

##### *Benzantialdoxime : Benzsynaldoxime.*

0.121 gram (1 milligram-mol.) in 100 c.c. ether.

Thickness of layer of solution in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to..... Complete absorption beyond.	3323	3009
20	Spectrum continuous to..... Complete absorption beyond.	3354	2981
15	The same.		
10	The same.		
5	Spectrum continuous to..... Complete absorption beyond.	3363	2973
4	Spectrum continuous to..... Complete absorption beyond.	3374	2963
3	The same.		
2	Spectrum continuous to..... Complete absorption beyond.	3385	2954
1	Spectrum same as above. Very faint indication of lines at $1/\lambda$ 3471 and 3491.		

0.121 gram in 500 c.c. ether.

Thickness of layer of solution in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to ..... Complete absorption beyond.	3568	2802
3	Spectrum continuous to ..... Line at $1/\lambda$ 3638.	3568	2802
2	Spectrum continuous to ..... Line at $1/\lambda$ 4417. Complete absorption beyond.	3638	2748
1	Spectrum continuous to ..... <b>Absorption band</b> Strong lines of spectrum from $1/\lambda$ 4321—4530.	3638 3638 to 4321	2748 2748—2314

0.121 gram in 2500 c.c. ether.

Thickness of layer of solution in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to ..... <b>Absorption band</b> Strong lines of spectrum, $1/\lambda$ 4306—4542.	3894 3694 to 4306	2707 2707—2322
3	Spectrum continuous to ..... <b>Absorption band</b> Strong lines of spectrum, $1/\lambda$ 4248—4555.	3824 3824 to 4248	2615 2615—2354
2	Spectrum continuous to ..... <b>Absorption band</b> Weak spectrum beyond $1/\lambda$ 4115—4555.	3886 3886 to 4115	2573 2573—2430
1	Spectrum almost continuous, but weak in position of absorption band, i.e., $1/\lambda$ 3902—4115.		

We have to express our thanks to Mr. R. S. Finlow, B.Sc., of the University College of North Wales, Bangor, for his assistance in preparing the substances referred to in this paper, and in photographing their spectra.





## BUNSEN MEMORIAL LECTURE.

(DELIVERED ON MARCH 29TH, 1900).

By SIR HENRY ROSCOE, B.A., Ph.D., D.C.L., LL.D., D.Sc., F.R.S., Hon. M.D. (Heidelberg), Corresponding Member of the French Academy of Science, Emeritus Professor of Chemistry in Victoria University, Vice-Chancellor of the University of London.

THE death of Bunsen at Heidelberg on August 16th, 1899, severs the last link connecting the chemists of our time with the great men of the earlier part of the century. With Berzelius, of whom Bunsen writes as "my truest friend and counsellor who, during the whole of my scientific life, has stood to me in intimate personal relationship;\* with Gay-Lussac, in whose laboratory in Paris he worked in the year 1833; with Dumas, whose acquaintance and friendship he enjoyed when they both were young; with Liebig and Wöhler, who were more nearly his contemporaries, and for whom throughout their lives he entertained the warmest feelings of affectionate regard; with the Berlin chemists Mitscherlich and the two Roses, as well as with the older physicists Dove, Wilhelm Weber, and Magnus, all of whom he counted among his personal friends.

Moreover, living to the ripe age of 88, he was destined to witness the deaths as well as the scientific births of many distinguished colleagues and pupils: of Kirchhoff, Helmholtz, Kopp, and Hofmann; of Strecker, Kolbe, Kekulé, Pebal, Lothar Meyer, and, lastly, of his successor in the Chair of Chemistry at Heidelberg, Victor Meyer. So that, in his later years, Bunsen stood alone in his glory, like some strong oak in the forest which still holds firm root unmoved by the tempests which have smitten down both old and young around it.

Nearly twenty years ago I gave, in the columns of *Nature*, a sketch of the scientific work of him whose memory we are here assembled to honour, as being not merely one of the most distinguished of the great chemists of the century, but one of the truest and noblest of men. In introducing the subject to the readers of that journal, I used the following words, which I make no apology for quoting, as I cannot find more appropriate expressions wherewith to commence the more detailed account of the life and labours of Bunsen in the

\* Berzelius, on his side, fully appreciated Bunsen's character and abilities. In 1844 he writes to Schönbein *à propos* of the latter's ozone experiments: "You must devote all your time to this so important investigation, you must follow it up with the true perseverance of a Bunsen, and if possible not abandon it until we are perfectly clear about it." (*Kahlbaum Briefwechsel*, Berzelius-Schönbein, 1898, p. 60).

Memorial Lecture, with the preparation of which the Council of the Chemical Society has honoured me.

"The value of a life devoted to original scientific work is measured by the new paths and new fields which such work opens out. In this respect, the labours of Robert Wilhelm Bunsen stand second to those of no chemist of his time. Outwardly, the existence of such a man, attached, as Bunsen has been from the first, exclusively to his science, seems to glide silently on without causes for excitement or stirring incident. His inward life, however, is on the contrary full of interests and of incidents of even a striking and exciting kind. The discovery of a fact which overthrows or remodels our ideas on a whole branch of science; the experimental proof of a general law hitherto unrecognised; the employment of a new and happy combination of known facts to effect an invention of general applicability and utility; these are the peaceful victories of the man of science which may well be thought to outweigh the high-sounding achievements of the more public professions."

Owing to the fact, not common in the annals of scientific intercourse, that I have enjoyed the privilege for nearly half a century of counting Bunsen amongst my most intimate friends, that we have stood in the position first of pupil and master, and afterwards of colleagues and co-workers, I am in the fortunate position of being able to present to you on this occasion something more than a description of the scientific work which he accomplished, the record of which any one who cares to do so can gather up from his published memoirs. From my personal recollections, I propose to lay before you a picture, doubtless imperfectly, but so far as my abilities go, truly drawn, of the man working in his laboratory, lecturing to his students, and enjoying simple but refined social intercourse with his friends. I shall hope to give you an idea what manner of man he was, what was his moral, as well as his scientific, character, to point out why he was not only venerated as a great leader and teacher, but why he inspired all with whom he came in contact with feelings of deep attachment and regard.

But first let me shortly mention some few particulars of his life, and give you a summary of his most important investigations. Bunsen was born at Göttingen on March 31, 1811. His father, Christian Bunsen,\* occupied the position of chief University Librarian and Professor of Modern Philology. After passing through the usual course in the gymnasium at Holzminden in Hanover, Bunsen entered the University in 1828, studied chemistry under Stromeyer (the discoverer of cadmium), obtained his degree in 1830, presenting for this purpose a thesis having the title "*Enumeratio et descriptio hygro-metrorum.*" He then visited Paris; arriving there at the latter end of

\* Born at Frankfort on April 1, 1770; died March 24, 1837.



September 1832, he remained until the spring of 1833, meeting Reiset, Regnault, Pelouze, and Despretz. The latter proposed to Bunsen to work in common at some problem in physical chemistry. Subsequently having visited Berlin and Vienna, continuing his studies and making acquaintance with the scientific men of those cities, Bunsen returned to Göttingen, where, in 1834, he was admitted by the University as Privatdozent in chemistry. In this position he lectured for three semesters, and after Stromeyer's death in 1835, Bunsen temporarily took up his work and lectured six days a week on theoretical and practical chemistry. In January 1836, he was appointed teacher of chemistry in the Polytechnic School of Cassel as Wöhler's successor. In October 1839, he became Professor Extraordinarius of Chemistry in the University of Marburg, and in 1842 was advanced to the position of Professor Ordinarius. Remaining here until 1851, he went for a short period to Breslau, and in 1852 accepted the chair at Heidelberg, vacated by Gmelin, a post which he occupied until his retirement in 1889. In these several positions, Bunsen laboured incessantly and devotedly for 56 years in the furtherance of chemical science, with the result that his name will be handed down to posterity as one whose work has earned for him the very first rank amongst chemists of the nineteenth century.

On the present occasion, it is not possible to do more than to indicate the nature and extent of Bunsen's work, so numerous are his published investigations, and so wide and far reaching their scope. To bring before you the general effect of the work, and to give you by some examples the special characteristics of that work, is all that can be now attempted. And for these objects I propose to treat the matter rather by classifying his work under separate heads of subjects, than by taking it in the chronological order of publication.

But before commencing a review of some of his most important researches, it may be well briefly to refer to the early work by which he won his scientific spurs. The first paper was one of general interest, as recording his discovery that freshly precipitated hydrated ferric oxide acts as a powerful antidote to arsenical poisoning by rendering the arsenic insoluble both in water and in the secretions of the body. This result of the withdrawal of the whole of the arsenic from solution by this means forms a striking lecture experiment (*Journ. de Pharm.*, 1834, 20, 567; 1838, 24, 93).

His next communication shows the interest which, in those early days, Bunsen took in mineralogy and chemical geology, subjects in which he, in after life, became a distinguished exponent. It consisted of an exact analysis and a detailed description of a specimen of allophane from a lignite bed near Bonn (*Pogg. Ann.*, 1834, 31, 53).

A more specially chemical subject next engaged his attention, namely, an investigation of a new series of double cyanides, in which he not only determined their composition with exactitude but showed the relationships existing between these and other well known members of the same class of bodies. He measured their crystalline form, and proved that ammonium ferrocyanide is isomorphous with the corresponding potassium salt (*Pogg. Ann.*, 1835, 34, 131; 1835, 36, 404; 1836, 38, 208.)

All this work was, however, merely of the nature of what he was in the habit of calling "ein kleiner Vorversuch" when he was indicating the manner in which a pupil should commence an investigation.

The first research in which Bunsen showed his power was the classical one on the cacodyl compounds—begun in Cassel in 1837, and continued in Marburg for no less than six years. The publication of this work placed Bunsen at once in the front rank of experimentalists.

To assist in forming an estimate of the scientific value of these researches (*Pogg. Ann.*, 1837, 40, 219; 1837, 42, 145; *Annalen*, 1841, 37, 1; 1842, 42, 14; 1843, 46, 1), it may be well to summon to our aid the opinion of a contemporary whom Bunsen himself, as we have seen, considered as a master, both from a philosophical and from an experimental point of view, the great Swedish chemist, Berzelius.

Those who have studied his celebrated *Jahresbericht* will know that Berzelius was unsparing in his criticism of inaccurate work and of illogical conclusions. The more valuable, therefore, and reliable are his remarks when favourable to the subject under review.

In 1839 (*Jahresber.*, 1839, 18, 487), Berzelius writes: "An extremely important discovery has been made by Bunsen, in the investigation of the well known fuming, self-inflammable liquid (Cadet's fuming arsenical liquid) obtained when anhydrous acetate of potash is distilled with arsenious acid. From this body, Bunsen has prepared several substances whose properties resemble those of an organic compound, in which, however, arsenic enters as an elementary constituent."

Of the importance of this research as affecting chemical theory, Berzelius reports (*Jahresber.*, 1841, 20, 526): "In the last German edition of my handbook, I gave what I considered the probable theoretical views regarding this substance, namely, that it contains the compound radicle  $C_4H_{12}As_2$ , similar to the radicles contained in organic bodies, for which I have suggested to Bunsen the name *kakodyl* in consequence of the nauseous smell of its compounds. With regard to this name, Bunsen writes me as follows: 'The view

of the existence of a ternary radicle  $Kd = C_4H_{12}As_2$ , agrees so perfectly with the behaviour of the whole alkarsin group that it would be scarcely possible to find a more striking example of a compound radicle. Alkarsin is kakodyl oxide,  $Kd$ ; it can be directly oxidised and deoxidised. Alkargen is kakodylic acid,  $Kd'$ ."

In a further notice (*Jahresber.*, 1842, 21, 503), Berzelius writes: "By this investigation Bunsen has made his name memorable. Chemical science is bound to acknowledge its debt to him for the investigation of a subject at once so important and so dangerous—an investigation of which it may well be said that it leaves little to be desired." Again he reports (*Jahresber.*, 1845, 24, 640): "Bunsen has now concluded his investigation on kakodyl. Through the private communications with which the author has favoured me, I have been able each year to give an account of the experiments as they progressed. The research is a foundation stone of the theory of compound radicles of which kakodyl is the only one the properties of which in every particular correspond with those of the simple radicles." And he concludes his criticism with a paragraph referring once more to the importance of this tedious and difficult research.

To quote another opinion, that of one of the leaders of modern chemical science, to place side by side with that of the great Swede, I would refer to that expressed by Adolf von Baeyer in his editorial remarks in the reprint of Bunsen's work in Ostwald's collection of scientific classics. "These researches have long been considered classical and they deserve such praise, particularly as pieces of model investigation demonstrating how the most difficult problems of experimental chemistry can be solved by a master's hand."

Amongst the many remarkable new facts which these researches contain is that of the non-poisonous properties of cacodylic acid, although it contains no less than 54 per cent. of soluble arsenic. "A solution of 8 grains of cacodylic acid injected into the *vena jugularis* of a rabbit produced no deleterious result on the health of the animal."

It is also of interest to read Bunsen's description of the properties of cacodyl cyanide, by the explosion of which he lost the sight of his right eye, was nearly poisoned, lying for days between life and death, but the investigation of which he nevertheless brought to a satisfactory conclusion. "It is obtained when cacodyl oxide is distilled with mercury cyanide, when it sublimes to a camphor-like solid; it melts at  $32.5^\circ$  to an oily liquid. The smell of this body produces instantaneous tingling of the hands and feet, and even giddiness and insensibility. The cacodyl compounds appear to exert a specific action on the nervous system. It is remarkable that when one is exposed to the smell of these compounds the tongue becomes covered

with a black coating, even when no further evil effects are noticeable."

Respecting the constitution of the radicle of the cacodyl compounds, various theories have from time to time been put forward. Bunsen himself did not give any opinion on the point, and it was Kolbe who first suggested the view that it was arsine-dimethyl,  $\text{As}(\text{CH}_3)_2$ , whilst the experiments of Frankland, and subsequently those of Cahours and Riche, rendered this probable. It is, however, to the researches of Adolf von Baeyer (*Annalen*, 1853, 107, 257), on the arsenmonomethyl compounds that we owe the full explanation of the relation which these various bodies bear to one another.

The cacodyl research claims our interest, not only because, as we have seen, it furnishes us with the first example of an isolable radicle, but also because it assisted Frankland and Kekulé in more exactly illustrating the term "chemical valency." For it is not too much to say that the subsequent researches of Frankland on the organo-metallic bodies, and on the so-called alcohol radicles, as well as those of the French chemists, and, I may add, those of Baeyer, received their first impulse from the cacodyl investigation. This indebtedness was acknowledged by our late lamented Fellow in the graceful and modest words which appear in the dedication of the volume of his collected researches.

"To my friend and teacher, Robert William Bunsen, whose researches on cacodyl, on the gases of the iron furnaces, and on the volcanic phenomena of Iceland, I have always regarded as models of investigation in pure, applied, and physical chemistry, I dedicate these pages both as a testimony of my regard, and in gratitude for the teaching whereby he imbued me with the necessity for thoroughness and accuracy in all scientific work. Would that they were more worthy of such a high standard."

Thus it is seen that although this remarkable research is the only one of any importance which was carried out by Bunsen in the domain of organic chemistry, it was destined to exert such an influence on the later developments of that branch of the science, that he may with truth be regarded as one of the pioneers of modern organic chemistry.

I now pass to an investigation of a different type, but one not less important or interesting than the last.

Up to the year 1838, when Bunsen began his investigation of the composition of the gases of the iron furnaces, the mode of measuring gaseous volumes and the methods adopted for the separation of the several gases was faulty and inaccurate in the extreme. But during the period elapsing between the above year and 1845, Bunsen had not only elaborated and perfected his well-known gasometric methods, but

had applied these methods with signal success to the investigation of the chemical changes which occur in the processes of a most important industry, that of the production of cast-iron in the blast furnace.

The first detailed description of Bunsen's gasometric methods was published in pamphlet form by Kolbe, who was at the time one of Bunsen's assistants. To the English public, these methods became known by a communication made to the meeting of the British Association at Cambridge in 1845 by R. W. Bunsen and Lyon Playfair, entitled "On the Gases evolved from Iron Furnaces with reference to the Smelting of Iron." Before entering upon the technical side of the question, the authors give experimental proofs concerning the accuracy and reliability of the methods employed for the measurement and the separation of the blast furnace gases. One of these consisted in the analyses of a large number of samples of air. These were collected and analysed in Marburg, and gave analytical results upon which Bunsen reports as follows:—"The close agreement of these experiments with one another, and with the result obtained by the careful experimental determination of the composition of air by Dumas, proves that the eudiometric examination of gases admits of a degree of exactness which is certainly not surpassed by the most minute chemical methods, and they further show that the presence of nitrogen does not exert any disturbing influence on the estimation of explosive mixtures of gases."

The report, printed in full in the British Association volume for 1845, next proceeds to discuss the experiments made by Bunsen on the composition of the gases evolved in the process of iron smelting in furnaces fed with charcoal and using cold blast at Vickerhagen, in Germany. From these, it appeared that in such furnaces nearly half the heat of the fuel consumed was evolved in the escaping gases.

The importance of these investigations, as being the first attempt to introduce accurate scientific inquiry into so widespread an industry as that of iron smelting, was at once appreciated by Lyon Playfair, who had made Bunsen's acquaintance at Marburg. In consequence, at Playfair's suggestion, Bunsen consented to visit England, and undertook to carry out a similar set of experiments for the English furnaces fed with coke and coal, and worked both by hot and by cold blast, to those which he had previously made in Germany. Thus was initiated a research which may be truly said to be a model of the application of the methods of scientific investigation to the elucidation of industrial problems. For not only did it clearly reveal the nature of the chemical changes which take place throughout the furnace, but pointed out the direction in which economies, to an undreamt-of extent, might be effected in the processes as then carried on. Thus it proved that whilst about half the fuel was lost as escaping

gas in the German furnaces, no less than 81.5 per cent. was lost in English ones, and, what was important from the industrial point of view, it pointed out that the whole of the heat thus allowed to escape might, without difficulty, be utilised for the various purposes of the works. These suggestions were only slowly adopted by the iron-masters; six years elapsed before any steps in the direction indicated were taken, but gradually the importance of the proposal was appreciated, and now and for many years past the whole of the hitherto wasted heat has been utilised, and economies effected of which the value may be reckoned by millions rather than by thousands of pounds.

Not only is it the lost heat which has been recovered, but also valuable bye-products, the existence of which had been, up to that time, entirely ignored. The report points out the loss of combined nitrogen—both as ammonia and cyanogen—which the process as then carried out evolves, the upper part of the furnace being, in the words of the report, “a region of distillation and not of combustion.” The amount of loss of these valuable materials was ascertained by accurate analysis, and a method for recovering them suggested, “without increasing the cost of manufacture or in the slightest degree affecting the process of smelting.” *À propos* of the determination of the escaping cyanogen compounds, the occurrence of a singular accident to Bunsen, as related by Playfair, is found in the admirable life lately written by Wemyss Reid. “Bunsen was engaged below,” at the blast furnaces at Alfreton, in Derbyshire, “and I above, passing the gases through water to collect any soluble products, when I was alarmed by being told that my friend had become suddenly ill. I ran down and saw white fumes coming out of a lateral tube, and Bunsen apparently recovering from a fainting condition. I applied my nose to the orifice and smelt the vapour of cyanide of potassium, which gave an entirely new light to the processes of the furnace.”

In 1857, Bunsen collected in a volume—the only book he ever published—the whole of his gasometric researches, and of this a second and greatly enlarged edition appeared in 1877 (“Gasometric Methods,” by R. W. Bunsen, translated by H. E. Roscoe, 1857). No better or more complete method of learning what Bunsen’s work is like can be taken than that of reading this volume. For originality of conception, for success in overcoming difficulties, for ingenuity in the construction of apparatus, and for accurate work, I believe the book, as a record of experiment, to be unequalled.

The first part contains a description of his various processes for collecting, preserving, and measuring gases, different methods being employed for the first of these according to the source from which the

gases are obtained, whether, as has been described, from blast furnaces, or from fumeroles, from volcanic vents, or when freely rising from mineral springs, or whether the gases are contained in solution in river- or spring-water. In the second part, we find a full description of the methods of eudiometric analysis, giving details of manipulation, with a discussion in each case of the probable sources of error and of the means of their limitation. As a model of accurate work (his oxygen determinations in air showed differences of 0.1 per cent. on the oxygen), Bunsen's eudiometric methods will always remain as the standard. More expeditious and simpler methods have been introduced of late years, but none of these equals the original processes in exactitude.

The third portion of the volume consists of a description of two new methods for determining the specific gravity of gases. The first of these, which also applies to the case of vapours, consists in weighing a tared vessel, filled first with the gas or vapour under examination and then with air, all variations due to change of temperature and pressure being eliminated by a simple and ingenious compensating arrangement. Perhaps the most interesting portion of this section is a description of a new thermostat, by means of which perfectly constant temperatures up to a high point can be obtained. This served Bunsen for ascertaining the specific gravity of aqueous vapour at different temperatures, and closely accordant numbers were obtained, although the weight of vapour amounted to only 80 mgm. The second method, applicable only to gases, depends on the determination of the rates of diffusion of the gases into air. Here, too, the volume of gas operated upon need not exceed 50—60 c.c., and yet the results obtained are extremely accurate. On this point, Bunsen remarks that for technical purposes, as, for example, for the determination of the density of coal-gas, the above simple method will probably be found preferable to all other processes.

The fourth part contains a series of investigations on the absorptiometric phenomena of gases in water and alcohol, the experiments having been chiefly undertaken with a view of determining the limits to which the well-known laws of pressure hold good. First he describes his absorptiometer, a new instrument by means of which it is possible to obtain accurate numbers with relatively small volumes of the gases. The absorption-coefficients of no fewer than 27 different gases in water and alcohol were determined by methods varying according to the nature of the case, partly carried out by himself and partly by many of his pupils, the result being that certain gases, generally those least soluble in water, are found to be in accord with Dalton's law of pressures and Dalton and Henry's law of partial pressures, whereas the more soluble gases are not always in accord with them. In the former

class, it is possible, from an experimental determination of the coefficient of absorption, to calculate the composition of the original gas, the composition derived from an absorptiometric analysis being found to agree exactly with that obtained by direct eudiometric measurements. It is also possible to ascertain whether a given gas consists of a single substance or is a mixture of several. Thus whilst eudiometric analysis cannot decide whether the gas evolved by the action of caustic alkali on an acetate is methane or a mixture of equal volumes of ethane and hydrogen, this can readily be accomplished by absorptiometric methods.

In the fifth part of the volume he discusses the phenomena of gaseous diffusion, and, although admitting the truth of Graham's law for cases of pure diffusion, he obtained results, when a stucco diaphragm of considerable thickness is used, which are not in accord with this law, the conclusion being that the pores of gypsum act upon gases, not as a series of fine openings, but rather as a series of capillary tubes, the phenomena being thus modified by those of transpiration. At the end of this chapter, he describes the details of a method for ascertaining, by diffusion, whether a given gas is a mixture or not.

The sixth and last section relates to the combustion phenomena of gases. The temperature of combustion, that is, the temperature of the interior of a mixture of burning gases, can be calculated from the heat of combustion of the gaseous mixture and the specific heats of the products of combustion under the assumption that the combustion at this high temperature is perfect. This condition, however, is not fulfilled, and Bunsen therefore endeavoured to determine this temperature by another means, namely, by measuring the pressure produced at the moment of explosion of an enclosed gaseous mixture.

For this purpose, he constructed a wonderfully simple apparatus, by means of which he ascertained that the maximum temperature of combustion of carbon monoxide and of hydrogen with the theoretical volume of oxygen was respectively  $3033^{\circ}$  and  $2844^{\circ}$ . He likewise attempted to determine the rate at which the explosion is propagated and came to the conclusion that for hydrogen and oxygen this was 34 metres per second. Subsequent experiments, especially those of Dixon (*Phil. Trans.*, 1893, 184, 97) have shown that this rate referred only to the initial period of the combination before the explosion wave had attained its maximum velocity, this latter amounting in the case of hydrogen and oxygen to the high number of nearly 3000 metres per second, the rate in other gases being of the same order in magnitude, and the ignition appearing to be propagated in somewhat the same manner as a sound wave.



One of the best known of Bunsen's discoveries is that of the carbon-zinc battery, which bears his name.

The construction of this battery in 1841 (*Annalen*, 1841, 38, 311) marks an era in the economic production of electricity. By the replacement of carbon for the platinum plates of Grove, Bunsen not only greatly reduced the initial cost, but increased the length of time during which the current can be maintained at its maximum. The success of the invention depends upon a method he devised for overcoming the disintegrating action on the carbon of concentrated nitric acid. This he effected by strongly igniting the cylinders, thus foreshadowing the process adopted on a large scale for graphitising the carbon poles now so generally used for electro-industrial purposes by ignition in the electric furnace. It is interesting to remember that it was Bunsen who, so early as 1843, pointed out that the electric current could be made use of as a means of illumination. He describes how, by using a battery of 44 of his elements, a light equal in illuminating power to 1171.3 candles can be obtained for an expenditure of 1 lb. of zinc per hour, and giving a light "the brilliancy of which the eye can scarcely support." He adds that by enclosing the carbon poles in a globe of glass, the wear of carbons by oxidation might be minimised. In short, he describes the first step towards the modern system of arc lighting rendered generally applicable on the large scale by the discovery of the dynamo. In his first communication respecting this battery, Bunsen gave a careful estimate of the work which it can accomplish. He showed that three cells will, in 30 minutes, decompose 0.6775 gram of water yielding 1137 c.c. of mixed gas measured at 0° and 760 mm. The corresponding loss of zinc in each cell was then determined, the result showing that the same weight was dissolved in each, and that the weights thus found correspond closely with the zinc equivalent for the above amount of water decomposed. A few years later, in 1848, he determined the electro-chemical equivalents for zinc and water. For the first of these, he obtained the value 0.033, and for the latter 0.00927; in other words, in order to decompose 1 mgm. of water per second, a current of the absolute intensity of 106.33 is necessary. These experiments confirm Faraday's law, showing that the quantity of water decomposed is proportional to the quantity of circulating electricity, and that the nature of the poles, as well as the conducting power of the liquids decomposed, exert no influence on the result.

We owe to Wilhelm Weber the first determination of the scientific units for electrical measurements, and in 1840 he obtained the number 0.009376 for the electrochemical equivalent of water with his unit-current. The difficulties which surround the subject are:

(1) the measurement of the current, and (2) the absorption of the decomposed gases by water and electrodes, and (3) the production of ozone. Bunsen improved the voltameter by evolving the mixed gases from hot acidified water by which the second and third of these difficulties were overcome. At present, voltameters depositing copper or silver are employed, and the ampère, which is now our practical unit, is one-tenth of that used by Weber and Bunsen, so that the electrochemical equivalent of water is 0.0009315 gram, meaning that one ampère decomposes that amount of water in one second.

This, however, was only the beginning of the work which the Bunsen battery was destined to perform. It was not until 1852, when in Breslau, that Bunsen turned his attention to using the battery for the electrolytic preparation of metals, some of which had not then been obtained in a coherent condition, and others had only been prepared in such minute quantities that their physical and chemical properties could not be properly studied. The first of these metals he attacked was magnesium (*Annalen*, 1852, 82, 137), the reduction of which had vainly been attempted by Davy, and only with very partial success by Bussy in 1830. The difficulty which had hitherto stood in the way, was the fact that the globules of molten magnesium are lighter than the fused magnesium chloride used as the electrolyte, and that on their formation they rise to the surface and burn. To avoid this, Bunsen adopted the ingenious plan of cutting the carbon pole, on which the metal forms, into pockets, inside which the magnesium is deposited, and from which the molten globule cannot escape. By means of the tangent galvanometer, Bunsen measured in absolute units the electricity employed, finding that the quantity of magnesium reduced is 2.45 grams, whilst the theoretical yield of metal is 4.096 grams. Having obtained the metal in some quantity, he determined its physical and chemical properties, showed how it could be pressed out into wire, and measured the luminous intensity of the burning metal. This he found to be 500 times that of a candle flame.

Some seven years later, he and I measured the actinic value of the light emitted by burning magnesium, and showed that it could be used for photographic purposes. We found that a burning surface of magnesium wire, which, seen from a point of the sea's level, has an apparent magnitude equal to that of the sun, effects, at that point, the same chemical action as the sun would do if shining from a cloudless sky at the height of  $9^{\circ}53'$  above the horizon. On comparing the visible brightness of these two sources of light, it was found that the brightness of the sun's disc, as measured by the eye, is 524.7 times as great as that of burning magnesium when the sun's zenith-distance is  $67^{\circ}23'$ , whilst at the same zenith-distance the sun's chemical brightness is only 36.6 times as great. Hence the value of this light as a

source of chemically active rays for photographic purposes is at once apparent. The application of magnesium as a source of light has become of technical importance. A burning magnesium wire of the thickness of 0.297 mm. evolves as much light as 74 stearin candles, of which five go to the pound. If this light lasted one minute, 0.987 m. of wire weighing 0.120 gram would be burnt. In order to produce a light equal to 74 candles burning for 10 hours, whereby 20 lbs. of stearin is consumed, 72.2 grams or  $2\frac{1}{2}$  oz. of magnesium would be needed. The light from burning magnesium has been employed for signalling, and for military and naval purposes, and it is especially used in pyrotechny.

Perhaps the most interesting of these applications of the battery is that of the preparation of the metals of the alkaline earths (*Journ. de Pharm.*, 1854, 26, 311; 1855, 28, 155), the isolation of which had hitherto eluded pursuit, and this work he handed over to our countryman, Augustus Matthiessen, who, under Bunsen's guidance, brought the investigation to a successful issue. The conditions most favourable to a reduction were carefully worked out. It had already been pointed out by Bunsen "that the density of the current (that is, the current per unit cross section) is the chief condition under which the electricity is able to overcome chemical affinities." This condition was fulfilled by using for the negative pole a very short length of thin harpsichord wire, upon which the reduced metal hangs in the form of molten beads, from which they can be quickly detached and plunged into petroleum. Another necessary condition is that the melting point of the electrolyte should be as low as possible, and this was attained by using a mixture of the chlorides of calcium and strontium, and by the addition of some sal-ammoniac to the mass as the electrolysis proceeds. This subject was again further elaborated, in 1875, in the Heidelberg laboratory by Hillebrand and Norton (*Pogg. Ann.*, 1875, 156, 466), who prepared considerable quantities of cerium, lanthanum, and didymium in the coherent metallic state.

But the reduction of the metals was not the only important work which Bunsen got out of his battery, for quite early in its history it made its mark in organic chemistry. If by the electrolysis of caustic soda we obtain oxygen and a metallic radicle, might not the electrolysis of an organic substance yield the corresponding organic radicle? Doubtless a question of this kind presented itself to Bunsen's mind when he set his assistant, Kolbe, to work on the electrolysis of acetic and valeric acids (*Annalen*, 1847, 64, 339; 1849, 69, 257). The results of investigations thus commenced and carried out, both by Kolbe alone, and in collaboration with Frankland, and the still more prolific researches of the latter chemist, are matters of scientific history; it

is, however, not so generally recognised that they owe their origin to the Bunsen battery

In addition to the zinc-carbon-nitric acid battery, Bunsen also constructed a powerful thermopile of copper pyrites and copper (*Pogg. Ann.*, 1864, 123, 505); and in later years a constant zinc-carbon-chromic acid battery (*Pogg. Ann.*, 1875, 155, 232) so arranged that the zinc and carbon plates could be lowered readily into the exciting liquid, and thus the battery was easily put in and out of action. This he used for obtaining the spark spectra of the rare earth metals.

For the purpose of measuring the intensity of the light given off by carbon-poles connected with his battery, Bunsen, in 1844, constructed his well-known photometer (*Berzelius Jahresber.*, 1845, 24, 13). The essential feature of this apparatus is the 'disc' of paper having a greased spot in the centre, or having a greased circumference with an untouched spot in the middle. With regard to this, Elster relates the story that when he showed this arrangement to the late Emperor Frederick, then Crown Prince, the Prince remarked, "For the first time in my life, I now know the value of a spot of grease." In the original Bunsen photometer, a small flame burning in a closed box fixed on a pivot in the centre of a long board, illuminated the back of the disc, the relative luminous intensity of the two sources of light under examination being ascertained by moving them alternately backwards and forwards on each side of the disc until, in each case, the spot disappeared. This form of the photometer was afterwards modified by other observers, not, according to Bunsen, to its advantage, by omitting the small flame and box, and simply moving the disc backwards and forwards between the two fixed sources of light. Recently, Preece has proposed to reintroduce the principle of the original Bunsen arrangement of ascertaining the relative luminosity by always exposing the same side of the disc, and therefore eliminating the error arising from its translucency. In one form or other, the Bunsen photometer has, however, for many years been in general use, but recently it has been partially replaced by the shadow photometer.

In this connection, mention must be made of two important researches of a physical rather than of a purely chemical nature, and characteristic of the manipulative as well as of the intellectual power of the author. They refer to the ice- and the vapour-calorimeters.

As, by means of his battery, it was possible for Bunsen to prepare small quantities of the rare metals, so by help of his ice calorimeter (*Pogg. Ann.*, 1870, 141, 1) he was able to ascertain one of their most important physical properties. It was constructed in order to be able

to determine exactly the specific heats of substances which could only be obtained in small quantities, and to which the usual calorimetric methods were therefore inapplicable. Thus it became of the greatest theoretical importance to ascertain the specific heat of indium, of cerium, lanthanum, didymium, and germanium, and other metals which are only obtainable in small quantities. The principles of construction and mode of action of the ice calorimeter are so well known that a description of the instrument and its use is here superfluous. They were published in 1870, and by its means the atomic weight of indium and the formulæ of its compounds were rectified, whilst the doubts arising as to the formulæ of the compounds of other metals were eliminated. "Thus Bunsen largely contributed to the confirmation, and to the acceptance of the system of atomic weights now in use, and thereby to the rational classification of the elements depending on that system."\*

In 1887, when 76 years of age, Bunsen published the description of a new vapour calorimeter (*Ann. Phys. Chem.*, 1887, 31, 1), upon which he had for some time been engaged. It depends on the same principle as the one previously constructed by Joly (*Proc. Roy. Soc.*, 1886, 41, 352). The body whose specific heat has to be determined is hung by a fine platinum wire to the beam of a balance, then brought into saturated aqueous vapour at 100° and the amount of water deposited on the body whilst it is being heated is weighed in the vapour, this amount being directly proportional to the specific heat. This method gives very accurate results, and differs in some essential respects from that proposed by Joly. In this way, Bunsen determined the specific heat of platinum at different temperatures, that of glass, and of water enclosed in glass. This latter he found to be 0.9992 (Joly obtained as a mean result 1.0062). The originality of this idea, arrived at quite independently from Joly, and the degree of accuracy with which the whole research is worked out, must indeed be considered as a wonderful achievement of a man close upon 80 years of age.

In addition to the work which Bunsen did alone, I am bound to refer to the long and difficult series of researches on the measurement of the chemical action of light, in all of which I was associated with him. (*Pogg.*, 1855, 96, 373; *Phil. Trans.*, 1857, 147, 355, 381, 601; 1859, 149, 879; 1863, 153, 139). For this reason, I feel difficulty in criticising it. This difficulty is, however, somewhat removed if, for this Lecture, I simply quote the opinion of Richard Meyer as found in his 'Nachruf' of Bunsen, with an extract from Ostwald's "*Classiker*" with which he closes the notice, and as an illustration of Bunsen's literary

\* Stanislao Cannizzaro, Commemorazione del Socio Straniero. R. W. Bunsen, *Rendiconti d. R. Acad. dei Lincei*, 8 December, 1899. Roma, 1899.

style, add a few sentences of the introduction which he wrote to the fourth part of our photochemical researches.

"The year 1855 was rendered especially memorable, as in that year the first communication appeared of the photochemical investigations which Bunsen carried out together with H. E. Roscoe. These researches are considered by Ostwald simply as 'the classical example for all further researches in physical chemistry.'

"The investigation is founded on the discovery by Gay-Lussac and Thénard of the action of light on a mixture of equal volumes of chlorine and hydrogen, in which an intense illumination produces an explosive combination, whilst with a less intense one the combination proceeds more slowly. So early as 1843, Draper had made use of this property for the construction of an actinometer, to which he gave the name of tithonometer. This, however, first became a reliable instrument in the hands of Bunsen and Roscoe. Equipped with this instrument, they have determined the most important laws of the chemical action of light after overcoming extraordinary experimental difficulties. Subsequently they replaced this apparatus, in consequence of the difficulties attending its manipulation, by the much more convenient chloride of silver actinometer.

"The first point determined was that the chemically active rays are reflected and absorbed according to the same laws as the visible rays, and that their intensity diminishes as the square of the distance. The question as to 'whether energy is expended in the act of photochemical combination for which an equivalent amount of light disappears, or whether the action, like that of the liberation of a spring, is brought about by the chemical rays without any appreciable loss of light,' is decided in favour of the first view; the phenomenon is termed by the authors photochemical extinction.

"A second, very remarkable phenomenon, first pointed out by the authors, is that of chemical induction. This refers to the fact that the action of light on the sensitive mixture of chlorine and hydrogen does not begin in its full intensity, but that it slowly increases, until after the lapse of a certain time it attains its regular and maximum rate. A satisfactory explanation, much less a theory, of induction is as yet wanting. Lastly, it was proved that photochemical action depends solely upon the quantity of the incident light, and is altogether independent of the time during which the insolation takes place.

"The great and important influence which photochemical action exerts in organic nature, especially in plant assimilation, renders the application of photochemical measurements to meteorological and climatic phenomena of special interest. But the difficulties which surrounded such an application were enormous. In the first place, it was necessary to find a unit of absolute measurement for the chemi-

cally active rays. A flame of carbonic oxide which emits chemically active rays of great intensity, burning in air under carefully specified conditions, satisfied the requirement. It was found that whilst the variation of the chemical action of the light reflected from a clouded sky was subject to no recognisable law, that obtaining when the sky was cloudless, and when direct sunlight was employed, at once exhibited distinct relations. The curves of daily intensity thus obtained before and after noon were seen to be symmetrical throughout the day; in direct sunshine, these curves of course rise much higher than is the case in diffuse daylight, moreover, the considerable variation due to change of latitude was precisely calculated.

"The dependance of the chemical action on the wave-length of the incident light was carefully studied, the result being that the most intense action was exerted by the rays between the lines G and H of Fraunhofer; the curve falls sharply towards the red end of the spectrum, whilst it extends in the more refrangible portion far into the ultra-violet. Strictly speaking, this only applies to the mixture of chlorine and hydrogen, still experiment has shown that the same thing is to some degree true of many other sensitive substances, although the distribution of the chemical activity in the spectrum is a different one.

"This short account of the photochemical researches is far from doing them justice. 'In no other research in this domain of science do we find exhibited such an amount of chemical, physical, and mathematical dexterity, of ability in devising experiments, of patience and perseverance in carrying them out, of attention given to the minutest detail, or of breadth of view as applied to the grander meteorological and cosmical phenomena of nature' (Ostwald)."

[And now comes Bunsen's introduction :—

"The measureless store of energy which nature has amassed in the sun's body flows in an unceasing current as solar rays throughout the universe.

"The labour expended on the earth's surface in the maintenance of the animal and vegetable creation, and in the production of geological change, is derived, almost exclusively, from this source.

"Those of the sun's rays which vibrate most slowly, and form the red portion of the solar spectrum, including the rays visible and invisible which surround them, give rise by their absorption, more especially to the thermic actions observed on the surface of the earth, and in both the fluid zones which as ocean and atmosphere encircle the solid crust of our planet. These rays constitute the sources of heat which, in those grand processes of distillation and atmospheric deposit, have effected these vast transformations of the earth's crust, by the study of which we obtain some idea of the immensity

of the sun's action exerted during geological ages upon our globe.

"Of a totally different kind, on a scale less magnificent, but not less important, are the effects mainly produced by the more highly refrangible, and more rapidly vibrating, portions of the solar rays. These rays exert the most marked influence upon the chemical changes on which the vegetable world depends, and are therefore of the greatest importance as regards the character and geographical distribution of organic nature.

"Although the atmospheric phenomena regulating the amount and distribution of the chemical action of light on the earth's surface have not as yet been systematised to the same extent as the thermic, electrical, and magnetic phenomena of meteorology, the reason is not so much that their importance has been overlooked, as that the difficulties which surround an exact investigation of the subject have up to the present time proved insurmountable. . . . The light which the sun radiates into space during each minute of time represents a chemical energy, by means of which more than twenty-five and a half billions of cubic miles of chlorine and hydrogen may be combined to form hydrochloric acid" (*Phil. Trans.*, 1859, 149, 879).

Of all Bunsen's researches, the one which will undoubtedly stand out pre-eminent as time rolls on is that on Spectrum Analysis.

The most important discovery made by Bunsen during the short duration of his residence in Breslau was the discovery of Kirchhoff, who was then Professor of Physics in that University, and whose great ability the elder man at once recognised. No sooner had Jolly removed to Munich in 1854 than Bunsen took care that Kirchhoff should be his successor in the Heidelberg Chair of Physics. And thus came about that great twin research which has made the name of these men known through the wide world. To dilate upon the importance of the discovery is unnecessary; to follow out the growth of this branch of science in its height and depth and breadth is here impossible. All that can be now done is to indicate briefly the origin of the discovery and to refer to a few points in Bunsen's work which are of special interest to chemists. To begin with, let me give you in Bunsen's own words the account of Kirchhoff's great discovery—namely, the full explanation of Fraunhofer's lines in the solar spectrum, pointing the way to a knowledge of the chemical composition of the sun and fixed stars, and then of his own application of the principles of spectrum analysis to the examination of terrestrial

In a letter to myself,\* dated November 15, 1859, he writes:

\* A facsimile representation of the whole of this letter is inserted at page 536.



"At the moment I am engaged in a research with Kirchhoff which gives us sleepless nights. Kirchhoff has made a most beautiful and most unexpected discovery: he has found out the cause of the dark lines in the solar spectrum, and has been able both to strengthen these lines artificially in the solar spectrum and to cause their appearance in a continuous spectrum of a flame, their positions being identical with those of the Fraunhofer's lines. Thus the way is pointed out by which the material composition of the sun and fixed stars can be ascertained with the same degree of certainty as we can ascertain by means of our reagents the presence of  $\text{SO}_2$  and  $\text{Cl}$ . By this method, too, the composition of terrestrial matter can be ascertained, and the component parts distinguished, with as great ease and delicacy as is the case with the matter contained in the sun; thus I have been able to detect lithium in 20 grams of sea-water. For the detection of many substances, this method is to be preferred to any of our previously known processes. Thus, if you have a mixture of  $\text{Li}$ ,  $\text{K}$ ,  $\text{Na}$ ,  $\text{Ba}$ ,  $\text{Sr}$ ,  $\text{Ca}$ , all you need to do is to bring a milligram of the mixture in our apparatus in order to be able to ascertain the presence of all the above substances by mere observation. Some of these reactions are wonderfully delicate. Thus it is possible to detect  $\frac{1}{1000}$  of a milligram of lithium with the greatest ease and certainty, and I have discovered the presence of this metal in almost every sample of potashes."

The following letter contains the first announcement of his discovery of cesium. It was not until one month later (May 10, 1860) that the fact of the discovery was communicated to the Berlin Academy of Sciences:

Heidelberg, April 10, 1860.

"MY DEAR FRIEND,

"Weltzien went to Paris a week ago and pressed me to accompany him, but unfortunately I was unable to free myself from work which I had postponed until the vacation, and so I have been obliged to forego the pleasure of seeing you in Paris and to tell you how much I have been pleased with your investigation. Do not be annoyed with me, dear Roscoe, that I have done nothing with our light investigation. I have left everything untouched, because I have obtained full certainty, by means of spectrum analysis, that besides  $\text{K}$ ,  $\text{Na}$ , and  $\text{Li}$ , a fourth alkali metal must exist, and all my time has been occupied in endeavouring to isolate some compounds of the new substance. Where the presence of this body is indicated, it occurs in such minute quantity that I almost give up hope of isolating it unless, indeed, I am fortunate enough to find a material which contains it in larger amount."

On November 6, 1860, Bunsen describes to me his further work on the new metal as follows:

"I have been very fortunate with my new metal. I have got 50 grams of the nearly chemically pure chloro-platinic compound. It is true that this 50 grams has been obtained from no less than 40 tons of the mineral water, from which 2.5 lbs. of lithium carbonate have been prepared by a simple process as a bye-product. I am calling the new metal "cæsium," from "cæsius" blue, on account of the splendid blue line in its spectrum. Next Sunday I hope to find time to make the first determination of the atomic weight."

The rare combination of mental and manual dexterity characteristic of Bunsen is nowhere more strikingly shown than in the investigation of the cæsium compounds. From these 17 grams of cæsium chloride obtained as above described, he not only succeeded in preparing and analysing all the more important compounds, but in crystallising the salts in such a form that he was able to determine their crystallographic constants and then to supply all the necessary data for fixing the position of this new element and its compounds in relation to its well known relatives potassium and sodium.

All the world knows that shortly after his discovery of cæsium the birth of another new alkali-metal, rubidium \* (*Berlin Monatsk.*, 1861, 6, 273), was announced by Bunsen, and the application of spectrum analysis led, in other hands, to the isolation of thallium in 1861, indium in 1863, germanium in 1886, gallium in 1875, and scandium in 1879, but alongside of these came announcements of the discovery of other new metals whose existence was more than doubtful. Concerning these he writes to myself: "The frivolous way in which new metals are now discovered by dozens and sent forth into the world duly christened is certainly no gain to science; only later inquirers will be able to decide what remains new and serviceable out of this chaos of material."

I may here remind you that cæsium is not only interesting as being the first metal to have been discovered by spectrum analysis, but because, even before Bunsen's discovery, chemists had worked with cæsium salts which they had mistaken for potassium compounds, so closely do the properties of the two metals correspond. Plattner, in 1846, analysing a mineral from Elba termed pollux, could not bring his analysis to add up to 100 parts and was unable to explain the anomaly. After Bunsen had established the existence of cæsium, Pisani, in 1864, took up the re-examination of the mineral, and showed that the alkali-metal was cæsium, with an atomic weight of 131.9, and not potassium with one of 38.85, and thus accounting for the missing percentage.

\* *Aulus gellius notes Attica* II, 28, "Rubidius autem est rufus atrior et nigrore multo inustus."

In the Christmas vacation of 1863, an extraordinary accident, illustrating in a painful manner the close analogy which exists between the properties of the potassium compounds and those of rubidium, occurred in Bunsen's laboratory. It is thus described in a letter from Bunsen to myself:

"For a week I have been in a very depressed and sad state of mind owing to a fearful misfortune which has taken place in the laboratory. During my absence from Heidelberg in the Christmas holidays, a man employed there in cutting wood, in spite of previous warnings, inexcusably took his little son with him into the laboratory and allowed him to run about without proper supervision. The child seems to have put into his mouth an iron tube which had been used for the reduction of metallic rubidium by heating the carbonate with charcoal, and in which the explosive compound carbonic-oxide-rubidium had been formed. The result was that an explosion occurred, and although no mechanical wounding took place, the child's throat and roof of its mouth were fearfully burned, so much so that it died within twelve hours. You can imagine how much I have been affected by this accident, although, Heaven be thanked, no blame for want of caution can be attributed to me."

In 1875 (*Pogg. Ann.*, 1875, 155, 280, 366), Bunsen published a long investigation upon the spark spectra of the rare earths. He had constructed, and describes there, a new and convenient form of carbon-zinc chromic acid battery which was sufficiently powerful to give a small arc light or to work a large induction coil, and could be put in and out of action, so that it was made ready for instant use by lowering the carbons into the exciting liquid. By the help of this battery, Bunsen mapped the spark-spectra of the rare earths, the separation of which has proved to be a tedious and very laborious piece of work. An accident, almost pathetic in its incidents and somewhat similar to the well-known accident which happened to Newton's manuscript, occurred to Bunsen. He had just completed the above-named research and the finished manuscript lay upon his writing table. On his return from dinner one day, he found the whole reduced to ashes! It seems that a spherical water-bottle stood on his desk, and this, acting as a lens in the sunlight, was the cause of the disaster. Writing to me on June 3, 1874, he says:

"You have good cause to be very angry with me for not having answered your sympathetic letter before this; but I have not allowed myself lately to think of anything which would remind me of the loss of my burnt research. . . . I had finished the editing of a memoir on a subject which had occupied me for three years, and was about to forward it to Poggendorff for publication, when on returning home the other day I found all these papers, which had caught fire during

my absence, reduced to ashes. The photographs of the apparatus, the drawings of the spark-spectra of the metals of the rare earths, to separate and map which had cost me untold trouble, all are burnt." With regard to this accident, Kirchhoff writes to me on May 22: "The disaster of which you read in the papers really happened. The manuscript of a research at which he had laboured for years, with maps of spectra, has been burnt. He was, to begin with, much depressed, but his wonderful elasticity of mind enabled him to overcome his dejection, and he has already begun to replace what was lost." This he continued to do, never drawing rein until the memoir was again ready for press.

The original views of Bunsen and Kirchhoff concerning the nature of the spectra of the alkali and alkaline-earth metals as examined in the flame of the Bunsen burner has since their time undergone considerable modification. We now know that whilst the spectrum of potassium, sodium, cesium, rubidium, and lithium, produced when any compound of these elements is brought into the flame, is that of the metal, it is quite otherwise with the similar spectra of the alkaline earths, for if a bead of calcium, strontium, or barium salt be brought into the flame, bright lines and bands are seen characteristic indeed of the individual substance, but differing altogether from the spectra obtained from the above compounds at the high temperature of the electric spark. In the first case, we are dealing with the spectra of a compound, whereas in the latter instance we obtain the line spectrum of the metal itself. Nor must it be forgotten that Bunsen was the first to point out that which has only in recent years been fully recognised, namely, that change of physical condition under which a spectrum is observed may give rise to fundamental changes in the character of the spectrum itself. It was in his research on the absorption spectrum of didymium (*Pogg. Ann.*, 1866, 128, 100), carried out with minute care, that this point was made clear. In this he proved that, examined under a high dispersive and magnifying power, a crystal of didymium sulphate gives an absorption spectrum in which the dark bands vary in position and in breadth according to the position of the crystal in regard to its axes through which the light passes, that is, whether the polarised ray is ordinary or extraordinary. These changes, somewhat similar to those since shown to be effected by change of pressure under magnetic influence, or from change of temperature, have yet to receive a satisfactory explanation. To enlarge upon these matters is, however, beyond the province of the present address, suffice it to say that Bunsen's original investigation has opened out an unbounded field for research the cultivation of which has already yielded great results and will in future yield still greater ones.

Next let us turn to his celebrated researches on chemical geology, especially those concerning the volcanic phenomena of Iceland.

The only relaxation from his scientific labours which Bunsen throughout life allowed himself was travelling, and this he thoroughly enjoyed. During many autumn vacations, I had the pleasure of accompanying him in rambles throughout Switzerland and the Tyrol. He walked well and had a keen appreciation of natural beauty, especially of mountain and woodland scenery, whilst he took great interest in the geology and physical characteristics of the districts through which he passed, and this it was that led him to turn his mind to chemico-geological studies. So early as 1844, in company with Pilla and Matteucci, he visited and carefully examined the carboniferous deposits occurring in the well known fumerole districts of the Tuscan Maremma (*Annalen*, 1844, 49, 264), and in 1846 he undertook his journey to Iceland, where he spent 3½ months, and the outcome of which was the well-known series of investigations on the volcanic phenomena of that island (*Annalen*, 1847, 62, 1; 1848, 65, 70). No doubt it was the eruption of Hecla in 1845 which served as the incentive to this expedition, for he desired, not only to examine the composition of the Icelandic rocks, which are entirely of volcanic origin, but especially the pseudovolcanic phenomena which present themselves in greater force immediately after a period of activity than at other times.

The expedition to Iceland was an official one promoted by the Danish Government. Bunsen was accompanied by Sartorius von Waltershausen and Bergman, both colleagues at Marburg, as well as by the French mineralogist Des Cloizeaux. They left Copenhagen on May 4, 1846, reaching Reykiavik after a short but stormy passage of 11 days. The party spent 10 days at the foot of Hecla, where Bunsen collected the gases emitted by the fumeroles, and investigated the changes which these gases effect on the volcanic rocks with which they come into contact. Eleven more days were given to the investigation of the phenomena of the geysers, and at the end of August Bunsen left the island, having in the short space of about three months collected a mass of material the working up of which, as he writes to Berzelius, "will tax all my energies for some length of time," a prediction which was subsequently fully realised.

Connected with the Icelandic expedition, the following story is told :—Bunsen had made all his arrangements for the expedition, had packed all the apparatus required for carrying on an experimental research in those regions, but he had been unable to obtain from the Kurfürst of Hesse-Cassel, of whose Civil Service he was a member, leave of absence from his professorship, although the application had been made repeatedly. In this difficulty, he appealed for help to a

cousin who happened to be domestic physician to this Prince, whose eccentricity was well known. The difficulty was solved as follows: the physician informed his Royal Highness that a cousin of his who was professor of chemistry in the Marburg University had conceived the wild idea of voyaging to Iceland, and that this was regrettable inasmuch as the professor would inevitably lose his life in so dangerous an undertaking, consequently he hoped that his Royal Highness would not accede to the request. The result of the interview was that the documents so long waited for were in Bunsen's hands next day!

Although some of the conclusions drawn by Bunsen from his investigations on the composition of the Icelandic rocks are not generally accepted at the present day, yet geologists admit that these researches laid the foundation of modern petrology, and that the original views which he therein expressed mark an era in the history of geological theory. It is now acknowledged that the idea which he was the first to propound, namely, the necessity of examining the chemical composition of eruptive rocks taken as a whole, rather than the determination of their various constituent minerals, must be carried out if we wish to come to an understanding as to their mode of formation. For this purpose, he made an extensive series of complete analyses of the Icelandic rocks. And from these results he drew the remarkable conclusion that in Iceland, and probably in most of the larger volcanic systems, there exist two extreme types of rocks. One of these, richest in silica, is termed the "normal trachyte"; the other, containing less silica and naturally more basic constituents, is the "normal pyroxene." All the Icelandic rocks can be classed as being either one or other of these normal silicates, or as admixtures of the two. In order to account for these well established facts, Bunsen supposed that the two normal types were separated out from the mass of molten silicate in the interior of the earth at distinct points. And he founded this supposition on the fact of the influence of pressure on the melting point (*Pogg. Ann.*, 1850, 81, 562).

This had been independently pointed out by James Thomson, in 1849, as being a corollary of the mechanical theory of heat, and had also been experimentally verified by William Thomson (Lord Kelvin) in the case of water. Bunsen developed this point further by proving that, exposed to a pressure of 156 atmospheres, the temperature of solidification of spermaceti was raised from  $47.7^{\circ}$ , under ordinary atmospheric pressure, to  $50.9^{\circ}$ . As volcanic rocks must have been subjected to varying pressures amounting to many thousands of atmospheres, it is clear that the effect of such variation on the point of solidification of the rocks must be very considerable, and that where the pressure

Facsimile.

Wittellberg, d. 15. Mai 1889.

Mein lieber Herr, Sie  
wären, für Ihren letzten  
us Ihre Gabe, können  
nicht sondern mir sehr wichtig  
und interessant. Daß Sie  
unsern vortierischen Schreibe-  
werkzeug bedeutende Entdeckungen  
Herk gefunden hat, halte  
ich für ganz ungewöhn-  
lich nach unseren früheren  
Versuchen und nach denen,  
die ich noch angefordert habe.  
Ich ersuche Sie, durch Einsenden  
des Papiers auf der Reinigungs-  
zu erhalten. Bei dessen Fortschreiten

und meinen letzten Versuch  
war aber die Dauer der Dopplung  
gegen die der Verdampfung  
jetzt nicht selten <sup>aber</sup> wie  $\frac{1}{500}$  Sekunden  
zu 20 Sekunden. Nimmt man  
nun an, dass die Verdampfung  
bei dem Chlorätherpapier  
sehr schnell überwunden  
wird, so müssen Dopplungen  
bei Ihren Versuchen nicht  
mehr sichtbar werden,  
wahrscheinlich bei der  
notwendigen Schmelzezeit  
her wird, möglich.  
Mit dem neuen Apparat,  
den ich Ihnen sende



mit uns daß Alles leicht  
ermittelbar Capen, Jede  
ist das Mutter der Art, daß  
ich alle Konow ganz auf  
auf besser Zeit haben  
aufpassen müssen. In den  
Meinhardt - oder Opferfeme  
denke ich mit. diesem Augen  
alles erreicht zu haben, was  
so lang vergeblich auf  
Krebs haben. Im Augen-  
blick bin ich mit Knochstoff  
mit einer Gemeinschaft, die  
Arbeit beschäftigt, die es  
nicht schlafen läßt. Thorpe  
hat nehmlich eine wunder-  
schöne



ganz unerwartete Entdeckung  
... ist die  
Koralle der Lande  
Linien im Sonnenspektrum  
aufgefunden sind die  
Linien Knopflinien im  
Sonnenspektrum verfahren  
mit in Linienlosen  
Flammenspektren heraus  
gebracht hat und zwar  
der Lage nach mit  
den Fraunhofer'schen  
Bezeichnungen.

Man darf nun gehen,  
die Knopflinien zusammen  
setzung der Sonne mit

der Fipfferne mit derselben  
Sicherheit zu gewinnen wie  
wir es bei der Sonne  
Messungen bestimmen. Auf  
der Erde haben wir die Stoffe  
nach dieser Methode mit derselben  
Schärfe untersuchen und nach  
meiner, wie auf der Sonne  
so daß ich z. B. in 20 Grm.  
Mennige noch einen Lithion  
gehalt habe nachweisen  
konne. Ihre Erwartung  
Mancher Stoffe ist durch  
Methode allein nicht  
möglich vorzugehen.  
Haben Sie ein Instrument  
Li Ka Mi Ba Sr Ca, so brauchen  
Sie nur ein Meßinstrument.



is less the composition of the crystalline mass would be different from that of the rock formed where the pressure is greater. This remarkable theory of the existence of two distinct types of rocks separating out from the same fluid mass, has recently been supplanted by other views, but the facts respecting the composition of the eruptive rocks upon which the idea was based will ever remain, not only a monument to the patience and perseverance of their discoverer, but as some of the most valuable additions to our knowledge of chemical geology.

Bunsen's investigations of the pseudo-volcanic phenomena\* of Iceland, and especially those of the great geyser, may, indeed, be considered as models both from a physical and a chemical point of view. The temperature experiments, which were both difficult and dangerous, were conducted by Bunsen in collaboration with Des Cloizeaux. He first shows that the cylindrical shaft, which is no less than 74 feet deep, and 10 feet in diameter, had been built up by the deposition of the silica which the water holds in solution, so that, in Tyndall's words, "the Geyser is the architect of its own tube." Bunsen determined the temperature of the water contained in the tube a few minutes before an eruption, and found that in no part of the tube did the water reach its boiling point. The situation at which the temperature of the water most nearly approached the boiling point under the superincumbent pressure, was about 30 feet from the bottom, reaching there  $121.8^{\circ}$ , whereas the boiling temperature was  $123.8^{\circ}$ , making a difference of only  $2^{\circ}$ . The question occurs, why, under these circumstances, does an eruption take place? This is satisfactorily accounted for by the fact that, owing to the existence at the base of the geyser tube of volcanic vents, through which steam under pressure is passing, the whole column of heated water is lifted, so that whilst originally at a point 30 feet from the bottom the temperature of the water was below the boiling point, when it became raised through a height of 6 feet by the pressure of the issuing steam, its temperature was  $1^{\circ}$  above the boiling point, the same being true for every point in the cylinder, and thus the ebullition gradually increased until at last it became eruptive. An experimental illustration of Bunsen's geyser theory is described by Tyndall in his well-known work.

The distinct shade of blue possessed by waters of the geyser led Bunsen to examine the colour of distilled water (*Edin. New Phil. Journ.*, 1849, 47, 95). For this purpose, he enclosed carefully purified distilled water in an horizontal tube 2 metres long, closed by plate-

\* An excellent English translation of the memoir "On the intimate connection between the pseudo-volcanic phenomena of Iceland" is found in the volume of *Reports and Memoirs* printed by the Cavendish Society in 1848.

glass ends, the interior of which had been blackened thus showing that the absorptive power of water is exerted less upon the blue than upon the other rays of the spectrum, and explaining the blue colour of certain lakes and rivers, and the colour of sea-water as observed in the Blue Grotto of Capri. The differences in depths of shades of blue possessed by waters in various places are doubtless due to the variation in size of the suspended particles varying in their reflective power.

Of a totally different character was the next piece of work to which I shall refer ; it related to the separation of the metals of the platinum group.

In 1868 (*Annalen*, 1868, 146, 265), Bunsen worked for some time on methods of separating the several metals contained in the residues left after the process of extracting the platinum as practised in the Imperial Mint at St. Petersburg. He fully describes the somewhat complicated processes by which he effected these separations ; (1) the elimination of platinum and palladium ; (2) the separation of ruthenium ; (3) the deposition of iridium and rhodium ; and (4) the chief aim of the research, the preparation of pure rhodium and its compounds.

In the course of these experiments, Bunsen met with a singular and unexplained accident, which fortunately had no serious consequences. With reference to this, he writes to me as follows :

"It is still difficult for me to write, as my hands are not quite healed, but I cannot longer delay replying to your sympathetic letter, as I fear you may be uneasy about me. The cause of the explosion is to me still quite inexplicable. I had prepared about a pound of the mixed metals rhodium and iridium by zinc reduction, and had dried the powder at 100° in a water-bath, when, on lightly touching the finely divided metal, which was not quite cold, with my finger, the whole suddenly exploded with the energy of rammed-in gunpowder. This is all the more puzzling, as I have often rubbed a powder of the same metals violently in a mortar in similar quantities without any explosion occurring ; I have also heated similar preparations to a redness *in vacuo* without any gas, and certainly without a trace of hydrogen, being evolved. My left hand, with the first finger of which I touched the mass, saved my eyes, as my face and eyes were only superficially burnt by the flames which penetrated through my fingers. My eyes are, with the exception of singed eyebrows and eyelashes, unhurt, and so the explosion will luckily leave behind no serious traces."

In the preceding communication on the platinum metals, Bunsen describes the well-known filter pump which now bears his name.

But in a later publication (*Annalen*, 1868, 148, 269) he gives further particulars of its construction and use. These are so well known that it is only necessary to say that it is, in fact, a Sprengel's pump in which a column of 28 inches of mercury is replaced by one of 32 feet of water. In this way, a flow of water down a pipe of the above length produces a vacuum perfect up to the limit of tension of the aqueous vapour, and under the diminished pressures thus brought about, all the processes of filtration and of the washing of precipitates can be carried out with much greater rapidity and perfection than is the case when working under the ordinary atmospheric pressure. Here, as in all his published work, Bunsen is precise and exact. To show the time-saving value of the process, he precipitates two equal volumes of chromium sesquichloride solution of known strength by ammonia; the one portion he treats in the ordinary way, the other by the filter-pump method, whereby he demonstrates that, treated by the latter process, the precipitate is completely washed in 1/13th part of the time needed by the old plan, whilst only 1/50th of the volume of wash-water is required. Such filter-pumps, furnished with mercury pressure gauges, are now found in every well fitted laboratory.

A somewhat simpler form of filter-pump, first described by Piccard (*Zeit. anal. Chem.*, 1865, 4, 45), is, however, now also very generally employed; this consists of a short glass tube attached to the water tap with an inner jet for the water and an outer air-tube, the rapid flow of water carrying down with it a sufficient volume of air—on the principle of the steam injector—to create a diminution of pressure which, although by no means so great as that effected by the filter-pump as described by Bunsen, is still sufficient for many purposes.

As another example of the far-reaching character of his work, a few words must be said about his experiments on the products of the firing of gunpowder.

The nature of the reaction taking place in the firing of gunpowder has attracted the attention of chemists from early years. The accuracy of the simple equation, which at one time was believed to express this reaction was, long ago, rendered doubtful by the observations of Gay-Lussac and Chevreul, but the first exact investigation of the composition, both of the gases and of the solid products of the explosion, we owe to Bunsen and Schischkoff (*Pogg. Ann.*, 1857, 102, 321). The points of importance which they ascertained were, in the first place, that a large number of salts, whose presence had hitherto not been detected, were shown to be normal constituents of the smoke and solid residue; and, secondly, that many other gaseous products besides carbon dioxide and nitrogen are formed.

The powder was burnt under ordinary pressure, and the maximum

temperature of combustion as well as the maximum pressure were determined. Since 1858, other investigators have taken up this subject, especially Abel and Noble, Berthelot, and Debus.\* All these elaborate and more recent researches bear out the conclusion arrived at by Bunsen and Schischkoff, namely, that it is not possible to give any simple expression for the reaction, the products not only being very numerous, but varying considerably in their proportion according to the conditions, especially the pressure, and, therefore, the temperature, under which the explosion takes place.

The invention which perhaps more than any other has popularised the name of Bunsen is that of his celebrated burner.

The Bunsen burner, to the discovery of which I shall refer later on, is not only important from the fact of its almost universal employment, but also because familiarity with its properties led Bunsen to elaborate a series of flame reactions of very wide applicability. In the communication published in 1866 (*Annalen*, 1866, 138, 257), he showed that the non-luminous flame of the burner could, with advantage, supplant the blow-pipe flame for many analytical purposes. He first describes the constitution of the non-luminous gas flame; next he examines the action of the high temperature of the flame on the emission of light from solid bodies placed in the flame, referring especially to the extraordinary luminous intensity of incandescent erbia, interesting as being the starting point for the enormous industry of the incandescent mantle. He also determines the melting points and the rate of volatility of many salts by means of small beads of material placed at the end of a thin platinum wire in the flame, the rate of volatilisation being ascertained by the microscopic measurement of the diminishing diameters, in given periods of time, of the molten globules. He next details a variety of original and most ingenious methods of detecting minute quantities of the metals and non-metals by the help of reactions effected in the flame. So delicate are some of these methods, as, for instance, that of the detection of gold, that its presence can be with certainty ascertained in one centigram of a sample of a tellurium ore containing only a few tenths of a milligram of the metal.

Another most characteristic contribution to analytical chemistry is the investigation of a method of general applicability, published in 1853 (*Annalen*, 86, 265), known as the iodometric method and consisting of the volumetric determination of free iodine by means of sulphurous acid, for which has since been substituted the more stable sodium sulphate. This method, as every chemist knows, is not only

As Bunsen's oldest pupils and friends, I am indebted for many of the facts of his life to the works of Cassel and Marburg.



largely employed in commercial analyses, as, for example, for the estimation of the amount of manganese dioxide in manganese ores and Weldon mud, but it also gives valuable assistance in the determination of interesting theoretical questions, as, for instance, by Bunsen in the separation of cerium and lanthanum, and in the estimation of the atomic weight of the former metal.

Bunsen also devoted much time and labour to the perfection and systematisation of the processes of mineral water analysis.

In 1871, he published a detailed account (*Zeit. anal. Chem.*, 10, 391) of the methods of analysis which he adopted and their results in an investigation, made on behalf of the authorities, which had occupied him for some years, on the chemical and physical properties of the mineral waters occurring in various parts of the Grand Duchy of Baden. These results he afterwards published in pamphlet form. They certainly constitute the most complete series of mineral water analyses existing, and serve as a model in this domain of analytical chemistry. It is interesting to remember that Victor Meyer, who acted at the time as his assistant, carried out a large part of the experimental work.

Having thus pointed out some of the main features of Bunsen's scientific achievements, I now turn to my personal recollections to give you an idea of what manner of man he was, and how he lived and worked.

My reminiscences of Bunsen date as far back as the year 1852. In the autumn of that year, I was introduced to him by Professor von Mohl, the father of the late Frau von Helmholtz, who was then Professor of International Law in the University of Heidelberg. Bunsen had just been called from Breslau to fill the Chair of Chemistry at Heidelberg in succession to Leopold Gmelin, best known to English chemists as the author of the great handbook translated by our late editor, Henry Watts, and published by the Cavendish Society. I shall never forget the first sight of the man who afterwards became one of my most intimate and valued friends, and to whom I owe more than I can tell. At that time, Bunsen was at the height of his powers, physical and mental; he stood fully six feet high, his figure was well knit and powerful, his manner was one of suave dignity, whilst his expression was that of great kindness and of rare intelligence. Nor did this first impression of his bearing and character ever change, much less lose force. On the contrary, the more intimate became my knowledge, the more had I cause to respect and admire him. His was a heart free from guile, guiding a temper equable and amiable. During my long and intimate friendship, I never heard him set down aught in malice, or express more than a mild and good-natured

remonstrance, as when, for instance, one of the "practicanten" had adopted some faulty method of analysis, the master would remark: "Mein Gott, wie konnten Sie so was thun!" His genial, yet quietly dignified, manner placed strangers at their ease, at once inspiring confidence and commanding respect. All saw in him a man worthy of esteem and safe to trust, whilst those who were favoured by his more intimate friendship knew that for true modesty and greatness of heart he was excelled by none; they feel that for them he was the "chevalier sans peur et sans reproche," and that his companionship, whether scientific or social, was something to be proud of, the recollection of which remains as one of the most fruitful as well as one of the pleasantest of their lives.

Considerate and generous towards the opinions of others, he held firmly to his own, which at times he did not fail strongly to express. Simple and straightforward, he disliked assumption and hated duplicity; single-minded and wholly devoted to his science, he abhorred vanity and despised popularity-hunting. Indeed, of so retiring a disposition was he, that it was difficult to get him to take part in public proceedings, and next to impossible to induce him to make any public utterance of either a scientific or of a social character.

Another and a remarkable trait in his character was his keen sense of humour. This gave a charm and a zest to his society greatly appreciated by his friends, but of all his witty sayings which passed from mouth to mouth as "Bunsen's last," none was ever tinged with ill-nature, for this was foreign to his whole being. A large and interesting collection of these "Bunseniana" might be made. Suffice it here to mention a few. When travelling with Kirchhoff and myself in England during the autumn of 1862, Bunsen was mistaken by a lady for his distant cousin, "the Chevalier" Bunsen. "Did you ever complete, sir, your great work on 'God in History'?" asked the lady. "Alas, no," replied Bunsen, "my untimely death prevented me from accomplishing my design." One of his assistants, engaged in rearranging the collection of specimens, came to him with a bottle containing quinine, and wishing to find out whether the Geheimerath remembered the formula for the alkaloid, asked him for it; Bunsen, who was, however, not to be caught by chaff, replied, "Wozu denn, Herr Doctor, sind die Handbücher?" Like many men who are engrossed in their special calling, Bunsen was often absent minded, and many good stories were current about the mistakes which he thus unwittingly made. He had a well known difficulty in remembering names; one day a visitor called who he knew quite well was either Strecker or Kekulé. During the conversation he was endeavouring to make up his mind which of these two gentlemen was his friend. At last he thought it was Kekulé, then he convinced himself that it was Strecker. At last, however, he decided

that it was really Kekulé. So when his visitor rose to take leave, Bunsen, feeling confidence in his latest conclusion, could not refrain from remarking, "Do you know that for a moment I took you for Strecker!" "So I am," replied his visitor in amazement.

His, too, was a most affectionate nature, and one may regret that this side of his character was never freely called forth by family life. For Bunsen, like Dalton, tried to explain this failing by saying that he could never find time to get married. And this loneliness, especially in later life, oppressed him, and he often felt his isolated position keenly. When bidding him good-bye after my summer visits to him, he would smile sadly and remark, "Jetzt verlassen Sie mich wieder in meiner Einsamkeit." The following extract, from a letter to myself, referring to a notice of his life and labours, which appeared with a portrait, in 1881, in the columns of *Nature*, indicates more clearly than any words of mine can do, this side of Bunsen's character :

"The kind things you say of me in *Nature* touch me the more, as I see in them the faithful expression of your old true friendship for me, which is one of the great joys of my old age. When one arrives, as I shall do in a few days, at one's seventieth birthday, one has only to live through a short span of bodily and mental decay. Standing as I do at that period of my life, I feel as keenly as ever how modest and contemptibly small is the amount which I have added to the building of science. In the years which I am rapidly approaching, one lives more in the recollection of past happy days than in the present; and to the most pleasure-giving of them belong those which for many years we spent in true friendship together."

As another touching illustration of his affectionate disposition, I may mention that when congratulated one day by a friend on his having received some high mark of distinction, he remarked, "Ah, the only value such things had for me was that they pleased my mother, and she is now dead!"

It may here be well to mention that, in the year 1881, a congratulatory address, accompanying a bronze statuette of Berzelius, from his old pupils, was presented to Bunsen on the occasion of the celebration of the jubilee of his doctorate.

A letter written to me on Nov. 3 in that year indicates the feelings of regard and affection which bound together the Professor and his students,

"MY VERY DEAR FRIEND,

"Please accept my most hearty thanks for all the kindness you have shown towards me on this occasion, which has been so exciting for me. Of all the friendly interest that has been shown, what gave me the greatest and most heartfelt pleasure were the con-

gratulations to which your signature bore witness, amongst those of so many old friends, and of the donors of the beautiful and artistic gift which I received from the hands of Baeyer on the fiftieth anniversary of my graduation.

"I and all friends will be glad to see you. I was absent from here on my anniversary day, hoping in that way to escape all official notice, but on my return I found so many tokens of kind interest that I scarcely see how it will be possible for me to answer each one separately . . . , and so I am beginning to feel very much exhausted after all I have been through; I long most heartily for your friendly visit, which will be the best medicine for me."

This flight of the principal actor in the scene is very characteristic of the man, and *à propos* of this Kopp writes to me in January 1882:

"We had expected you to be present at the Jubilee. Bunsen had secreted himself with a few intimate friends in Gugenheim on the Bergstrasse, he had noted the locality of his retirement on a card, which, in case of your arrival, my wife was privately to hand to you. Bunsen took the unavoidable in good part, and not wholly without pleasure. He is very fresh and well, apart from his nearly permanent bronchial catarrh; he grumbles much, and is therefore perfectly normal."

In 1887, the seventh centenary of the foundation of Heidelberg University was auspiciously celebrated. Bunsen invited me to be his guest during the ceremony. During the inaugural discourse by Kuno Fischer, which lasted more than three hours, Bunsen fell asleep, as well he might do, but a more than usually eloquent passage disturbed his rest, and he woke up with a start, and whispered to me: "I thought I had dropped a test-tube full of rubidium on to the floor!"

Nothing was more distasteful to him than the etiquette of the Court. Nevertheless, during these festivities at which the Grand Duke of Baden, the Prince of Prussia, and other magnificos were, of course, present, Bunsen became the cynosure of neighbouring eyes. The recipient of heaps of Orders of all kinds, from all quarters, he never exhibited them except when he went to Court, or was invited to meet his Sovereign. To be used on such occasions only, he kept an "Order" coat, a 'Frack' or tail coat, upon the breast of which he had stitched as many of the stars and crosses as it would comfortably hold. During the Jubilee, the Grand Duke held a Court in the castle, and presentations were made. Bunsen, who had already paid his *devoirs* to the Grand Duke's party, expressed his unwillingness again to go through the necessary formalities, but, after some persuasion on my part, he consented, hoping, as he said, to conceal himself

behind the crowd of officials and dignitaries of all sorts who thronged the hall in which the Royalties were assembled. So we walked together up to the castle, in evening dress, as the custom is, Bunsen wearing his 'Orders.' The streets through which the procession of magnates was to pass were filled to overflowing by a good-natured crowd, no military or even police being present to clear the way, so as the royal carriages came up the steep road leading to the castle, a block occurred, and, as luck would have it, that containing the Grand Duke, the Duchess, and the Prince of Prussia came to a standstill at the exact point where Bunsen and I stood endeavouring to make our way through the crowd. The Duke at once recognised the Geheimerath, and beckoned him to come to the carriage, and there and then they had a friendly chat, and I had the honour of being presented. As soon as the cortège moved on, I had a good laugh at Bunsen, who, endeavouring to escape from all notice and attention, was entrapped in this amusing fashion.

Let me next endeavour to give you a picture of the master working in his laboratory.

When he first came to Heidelberg in the summer of 1852, Bunsen found himself installed in Gmelin's old laboratory. This was situated in the buildings of an ancient monastery, and there we all worked. It was roomy enough; the old refectory was the main laboratory, the chapel was divided into two, one half became the lecture-room and the other a storehouse and museum. Soon the number of students increased and further extensions were needed, so the cloisters were enclosed by windows and working benches placed below them. Beneath the stone floor at our feet slept the dead monks, and on their tombstones we threw our waste precipitates! There was no gas in Heidelberg in those days; nor any town's water supply. We worked with Berzelius's spirit lamps, made our combustions with charcoal, boiled down our wash-waters from our silicate analyses in large glass globes over charcoal fires, and went for water to the pump in the yard. Nevertheless, with all these so-called drawbacks, we were able to work easily and accurately. To work with Bunsen was a real pleasure. Entirely devoted to his students, as they were to him, he spent all day in the laboratory, showing them with his own hands how best to carry out the various operations in which they were engaged. You would find him with one man showing the new method of washing precipitates so as to save time and labour, or with another working out a calibration table of a eudiometer, or with a third pointing out that the ordinary method of separating iron from aluminium is unsatisfactory and carrying out a more perfect process before his eyes. Often you would find him seated at the table

blow-pipe—the flame in those days was fed with oil—making some new piece of glass apparatus, for he was an expert glass blower, and enjoyed showing the men how to seal platinum wires into the eudiometers, or to blow bulb-tubes for his iodometric analyses. Maxwell Simpson, who worked with Bunsen in the fifties, tells me that one day he saw Bunsen blow a complicated piece of glass apparatus for a pupil, who quickly broke it; Bunsen then made him a second, which at once met with a similar fate; without a murmur, Bunsen again sat down to the blow-pipe and for the third time presented the student (who we will trust looked ashamed of himself) with the perfect apparatus. Then he would spend half the morning in the gas-analysis room, going through all the detailed manipulation of the exact measurement of gaseous volumes, and showing a couple of men how to estimate the various constituents of a sample of coal-gas, and pointing out the methods of calculating the results, and then leaving them to repeat the processes from beginning to end for themselves.

His manipulative ability was remarkable; his hands, though large and powerful, were supple and dexterous. He was amusingly proud of having a large thumb, by means of which he was able to close the open end of a long eudiometer filled with mercury and immerse it in the mercury-bath without admitting the least bubble of air, a feat which those endowed with smaller digits were unable to accomplish. Then he had a very salamander-like power of handling hot glass tubes, and often at the blow-pipe have I smelt burnt Bunsen, and seen his fingers smoke! Then he would quickly reduce their temperature by pressing the lobe of his right ear between his heated thumb and forefinger, turning his head to one with a smile as the "agony abated," whilst it used to be a joke amongst the students that the master never needed a pincette to take off the lid from a hot porcelain crucible.

Accuracy of work was the first essential with him—most of us learnt for the first time what this meant. Six weeks' work was spent on a single silicate analysis, but most of us contrived to keep two such analyses going at once, whilst an analysis of coal-gas occupied a week or ten days. Not that he was averse to quick processes, indeed many of his own investigations contain novel proposals for shortening chemical methods, but this was never done at the expense of accuracy.

After having learnt his methods of quantitative work, of silicate analysis, for example, and after having gone through a course of gas analysis, those of us who had already been more or less trained elsewhere, were set upon some original investigation. Lothar Meyer, who worked at the next bench to myself, being a medical student, was set to pump out and analyse the blood-gases; Pauli and Carius worked on gas-absorption, employing for this purpose Bunsen's recently in-

vented absorptiometer; Russell was set to work out a new method of sulphur determination in organic bodies; Matthiessen was put on to the electrolytic preparation of calcium and strontium; Schischkoff analysed the gaseous products of gunpowder fired under varying conditions; Landolt had to find out the composition of the gases in various portions of a flame, and I worked by myself in one of the monks' cells upstairs on the solubility in water of chlorine when mixed with hydrogen and carbonic acid, the object being to ascertain whether this gas obeys the law of Dalton and Henry.

These are only some of the investigations on a variety of subjects carried on in the old monastery by Bunsen's pupils under his supervision, and they indicate only a tithe of his activity; for at the same time he was engaged in investigations of his own—he always had two or three on hand at once.

When Bunsen accepted the Chair of Chemistry at Heidelberg, the Baden Government agreed to build him a new laboratory. This was accordingly done, the plans having been worked out by him to the smallest detail, and in the summer of 1855 the new laboratory in the Plöck Strasse was opened. The rooms were by no means so lofty as those of our more modern laboratories, and as students from all parts of the world streamed in in large and increasing numbers, the new building soon became inconveniently crowded, and many applications for working benches had to be refused.

Some short time before the opening of the new laboratory, the town of Heidelberg was for the first time lighted with gas, and Bunsen had to consider what kind of gas-burner he would use for laboratory purposes. Returning from my Easter vacation in London, I brought back with me an Argand burner with copper chimney and wire-gauze top, which was the form commonly used in English laboratories at that time for working with a smokeless flame. This arrangement did not please Bunsen in the very least; the flame was flickering, it was too large, and the gas was so much diluted with air that the flame-temperature was greatly depressed. He would make a burner in which the mixture of gas and air would burn at the top of the tube without any gauze whatsoever, giving a steady, small, and hot, non-luminous flame under conditions such that it not only would burn without striking down when the gas supply was turned on full, but also when the supply was diminished until only a minute flame was left. This was a difficult, some thought it an impossible, problem to solve, but after many fruitless attempts, and many tedious trials, he succeeded, and the "Bunsen burner" came to light. On the theory of the "Bunsen burner" I need not detain you, for it has already been brought before the Society in his usually clear and masterly manner by our President (this Journal,

1877, i, 31, 627). I may, however, here remark that so general, indeed so universal, has the use of this become that its name and value must be known to, and appreciated by, millions of the human race. Yet how few of these have any further ideas connected with the name of its author.

Another discovery which early brought him prominently before the public was that of the "Bunsen," or as he preferred to call it, the "carbon-zinc" battery, a description of which has already been given. The manufacture of either the battery or the burner might, had the inventor wished, have been so guarded as to bring in a large fortune. But Bunsen had no monetary ambition, although he fully appreciated the importance of applied science, and this is a fine trait in his character. He not only disliked anything savouring of money-making out of pure science, but he could not understand how a man professing to follow science could allow his attention to be thus diverted from pure research. "There are two distinct classes of men," he used to say, "first those who work at enlarging the boundaries of knowledge, and, secondly, those who apply that knowledge to useful ends." Bunsen chose the first—perhaps one may say the higher—part, and the notion of making money out of his discoveries, or of patenting any of them, never entered into his head. As illustrating this habit of mind, I remember that once we were talking about a former pupil of his, of whose scientific ability he entertained a high opinion. "Do you know," he remarked to me, "I cannot make that man out; he has certainly much scientific talent, and yet he thinks of nothing but money-making, and I am told that he has already amassed a large fortune. Is it not a singular case?" To which I replied that I did not find it so very remarkable!

In the new laboratory, research work was carried on with even greater activity than it had been in the old one. My own work on photochemical measurements was first carried out in a darkened chamber under the slates, where the summer temperature was usually above blood-heat, and afterwards in Bunsen's private room downstairs. Men whose names have long ago been household words with us came to work under the Master. Baeyer carried out his early work under Bunsen's care, though after a time he left to work with Kekulé, who had just set up a private laboratory in the neighbourhood. Lothar Meyer, Carius, and Landolt were continuing their several researches; Dexter worked on the atomic weight of antimony, Holtzmann on the cerium metals, whilst Pebal, Erlenmeyer, Meidinger, Lieben, Barth, Moritz Hermann, and Lotz each published interesting communications; and Bahr from Stockholm, Frapolli from Milan, Pavesi from Padua, and Lourenço from Goa were also occupied



in research. Most of this work Bunsen had initiated, all he assisted by co-operation and advice.\* Then, in addition, there were the beginners, to the number of 60 or 70, all of whom were looked after by the Professor and with some of whom he would spend hours showing them how to detect traces of metals by aid of the "flame reactions," or how to estimate the percentage of dioxide in pyrolusite by his iodometric method. So from Bunsen all who had eyes to see and ears to hear might learn the important lesson that to found, or to carry on successfully, a school of chemistry the professor must work with, and alongside, of the pupil, and that for him to delegate that duty to an assistant, however able, is a grave error.

How, it may be asked, could a man who thus devoted himself to supervising the work of others in the laboratory—and who, besides, had a lecture to deliver every day, and much university business to transact—how could he possibly find time to carry out experimental work of his own? For it is to be noted that Bunsen never kept an assistant to work at his researches, and unless co-operating with someone else, did all the new experimental work with his own hands.

It is true that in certain instances he incorporated the results of analyses, made by a student whom he could trust, into his own memoirs; notably this was the case with the silicate analyses which he used in his chemico-geological papers, and with many of the examples given in illustration of some of his new analytical methods. Then, spending the whole day in the laboratory, he was often able to find a spare hour to devote to his own work, of devising and testing some new form of apparatus, of separating some of the rare earth metals, or of determining the crystalline form of a series of salts.

Again the editing of the research, and the calculations, often complicated, which that involved, were carried on in the early morning hours. When, for four summers after the year 1857 I spent my vacations working at Heidelberg, I lived in his house, and although I rose betimes, I always found him at his desk, having begun work often before dawn.

Then, although he frequently travelled during the vacations at Easter and in the autumn, often, I am glad to remember, with myself as companion, he generally returned after a short absence to continue

\* During the twenty years following 1858 the following were amongst those who worked with Bunsen: Graebe, Ladenburg, Bütschli, Wichelhaus, Laspeyres, Richard Meyer, Victor Meyer, Crum Brown, Thorpe, H. Rosenbusch, Horstmann, Emmerling, A. Salkowski, Bunte, Guido Goldschmidt, Gibson, Smithells, Michael, Zorn, Bernthsen, Königs, Treadwell, Herzig, Fabinyi, Wanklyn, Phipson Beale, Cartmell, Long, Schischkoff, Andrejeff, Beilstein, Filipuzzi, Schneider, Dollfus-Ausset, Kündig, Goppelsroeder, Mayboom, Nessler, Winckler, Rose, Lucius, Friedländer, L. Mond, Sprengel, Messel, and lastly, Curtius, who at present occupies the Chair of Chemistry at Heidelberg.

an unfinished, or to commence some new, research, and during these quiet days much work was done by both of us.

I will now say a few words about Bunsen as a lecturer.

Bunsen lectured on general chemistry every morning in the week from 8 to 9 in the summer, and from 9 to 10 in the winter semester. The lectures were interesting and instructive, not from any striving after oratorical effect, or by any display of "firework" experiments, but from the originality of both matter and illustration. His exposition was clear, and his delivery easy, and every point upon which he touched was treated in an original fashion; no book, of course, was used or referred to; indeed, he avoided much consultation of handbooks, the only two which I have seen him occasionally turn to for the purpose of looking up some facts about which he had doubts were "Gmelin" and "Roscoe and Schorlemmer." When occasionally one of the 'Practiscanten' consulted him about a passage in some manual which appeared defective, he would laughingly remark that most of what is written in books is wrong.

The illustrative lecture experiments, which he invariably performed himself, were generally made on a small scale, were often new, always strictly relevant to the matter in hand, and never introduced for mere sensational effect. He paid much attention to these experiments, and after the table had been set in order for the particular lecture by the assistant, he would regularly spend half-an-hour, sometimes an hour, in convincing himself that all was in readiness and in rehearsing any experiment about the success of which he was not perfectly certain.

He used few notes, but it was his habit to write up any numerical data in small figures on the blackboard, and to refresh his memory with these when needed. When I attended the lectures in the early fifties, Bunsen used the notation and nomenclature of Berzelius, writing water  $\text{H}$ , and alumina  $\text{Äl}_2$ . Later on, he still employed the dualistic notation, writing  $\text{KOSO}_3$ ,  $\text{HOSO}_3$ , for  $\text{K}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ , indeed, I believe that he never adopted our modern formulæ or used Cannizzaro's atomic weights, although his determination of the atomic heat of indium and his work on caesium and rubidium were amongst the most important contributions towards the settlement of those weights.

Bunsen did not enlarge in his lectures on theoretical questions, indeed to discuss points of theory was not his habit and not much to his liking. His mind was eminently practical; he often used to say that one chemical fact properly established was worth more than all the theories one could invent. And yet he did much to establish the evidence upon which our modern theories rest.

On this point, the following statement, for which I am indebted to Dr. Gibson, who worked with Bunsen from 1873 to 1875, is of interest: "What was impressed" in Bunsen's lectures, "was not so much the theories concerning the elements and their compounds as the salient facts. The properties and behaviour of the elements were described with a clearness and wealth of experimental illustration that made their individuality and characteristics stand out in prominent relief compared with which such things as theories and formulæ were almost lost sight of. At a very early stage of the course, the greater part of two lectures was devoted to an analysis of mercuric oxide carried out before the class in the most precise and painstaking manner. The whole was a masterly exposition of analytical method involving a detailed but most lucid discussion of the various sources of error and of the two ways by which accuracy may be arrived at, namely, either by reducing these errors to a minimum or by estimating them and making the necessary corrections."

Concerning this side of Bunsen's character, and on the influence exerted by his work on chemical theory, I cannot do better than quote the judgment of Cannizzaro, who, in his eloquent *éloge*, uses the following words:

"Bunsen did not take any active part in the theoretical discussions which took place during that period of his scientific career, but he was not indifferent to the fundamental arguments of chemical science, that is, the atomic weights of the elements and the formulæ of their compounds. Whilst controversy raged, he was silently employed in collecting experimental data, and teaching how these can be best obtained in order to settle all pending questions. This was his true mission. And this he fulfilled admirably."

To this passage, Cannizzaro appends a note which is so characteristic both of the writer and of his subject that I venture to quote it:

"In 1860, whilst I was on my way to attend the Chemical Congress at Carlsruhe, which was convened in the September of that year by Weltzien, Wurtz, and Kekulé, I stayed for several days at Heidelberg, where I had an opportunity of discussing with Bunsen the questions which were to be raised at the Congress, namely, the choice of a system of atomic weights of the elements, and of the notation of their compounds. I found him well informed as to my published views on these subjects, which he had discussed with his intimate friend Kopp. He was satisfied with the attempt to effect an agreement between the conclusions drawn from atomic heat, isomorphism, and from the application of Avogadro's theory, but he did not enter seriously into the discussion, and in conversation on the subject he immediately reverted to an enumeration of the new experiments which ought to be made in order to settle doubtful points."

*À propos* of Bunsen's lectures, I may here relate a story which is characteristic of the man.

Although the motto of "Lehr-und Lern-Freiheit" is that of every German University, yet it is obligatory on all candidates for public appointments to bring up certificates, signed by the Professor, of attendance on specified lectures. Bunsen, considering this a matter of form, usually signed "mit ausgezeichnetem Fleiss," without further inquiry. On one occasion, however, looking at the applicant, he remarked, "Aber Herr Dingskirch ich habe Sie in die Vorlesung gar nicht gesehen." "Ja, Herr Geheimerath," replied the student, "ich sitze aber immer hinter die Pfeile." "Ach da sitzen so viele," was the only remark vouchsafed by the Geheimerath, who at once filled in the schedule, "mit ausgezeichnetem Fleiss!"

In conclusion, I may remark that Bunsen's constitution was a vigorous one, and it carried him fairly well through a long life; still, continuous exposure to the fumes and vitiated air of the laboratory induced bronchial troubles, from which in later life he suffered considerably. Beyond one sharp attack of peritonitis when travelling with Pagenstecher in the Balearic Islands, I do not think he ever had a serious illness. His habits were frugal, the only extravagance in which he indulged being his cigars. Of these he consumed a fairly large number, always having one or a part of one in his mouth; but as he generally allowed it to go out many times before he finished smoking it, the time it lasted was much above that of the average smoker.

Although taking no active part in German politics, Bunsen was a staunch Liberal; and no one rejoiced more than he on the consummation of the unification of the German people under the headship of the Emperor William. He was, however, no admirer of Bismarck's régime. On Mitscherlich's death, Bunsen received a very pressing invitation to become Mitscherlich's successor in Berlin. On this subject, he writes to me: "Very liberal offers with regard to Mitscherlich's professorship have been made to me, but I have declined them, as I did not wish to belong to the regiment of Herr von Bismarck, or to start again from the beginning with chemistry, the position of which had there fallen so low. In addition to that, they have here complied with the wishes which I had before expressed, and have offered Kopp a professorship here, besides raising the fund of my institute by a thousand gulden."

In 1889, Bunsen retired from active University life, resigning his professorship, and therefore his official residence, and retiring to a pretty little villa in "Bunsen Strasse" which he had purchased, where he spent the remainder of his days in quiet repose. His chief relaxation and enjoyment throughout his life in Heidelberg was to

wander with Kirchhoff or Helmholtz or some other of his intimate friends through the chestnut woods which cover the hills at the foot of which the town lies. As the infirmities of age increased and his walking powers diminished, he was obliged to take to driving through the woods along the charming roads which intersect the hills in all directions. Writing became a difficulty, and in his latter days the news of him came to me through our mutual friends Quincke and Königsberger. One of the last letters I received from him is dated June 4, 1890:

"... I have been suffering for weeks from the after-effects of influenza, and I am still so weak that I have to spend my days on the sofa, and have scarcely strength to walk the few yards to dinner at the Grand Hotel. When I think that next March I enter on my eightieth year, I must resign myself to the fact that such a state of things is inevitable. My hearing, too, becomes more and more difficult and my eyes are worse, so I have to deny myself all social intercourse, and only see now and then one of my old friends who comes to look me up. But in spite of all this, I can still feel the humour of life. This is, unfortunately, not the case with Kopp, who has just resigned his chair. He suffers constantly, but with his chronic hypochondriacal temperament he was unable to fulfil his professorial duties and feels very unhappy. I hope that in time he will resign himself to the inevitable. . . ."

Few men knew Bunsen so well, or admired him so much as Leo Königsberger, the distinguished professor of mathematics at Heidelberg. The following appreciative remarks contained in a letter to myself on Bunsen's mental constitution seem to me so true that I make no apology for here quoting them:

"Bunsen did not possess a mathematical brain in the sense so splendidly illustrated in the cases of Maxwell and Kelvin. He had, however, a logical mind, enjoying the rational analysis of recognised truths, and was thus able, thanks to the wonderful intuitive power of a great scientific man, and thanks also to his æsthetic character, to grasp and to understand rather than to explain phenomena. These, therefore, were rendered evident to him, not so much by an exact intellectual process, as by the evidence of the senses and by the gratification which their perception afforded. Quite otherwise was it with Kirchhoff, as he entered frequently and with zest even into unfruitful mathematical or philosophical speculations. It was always interesting to listen to these two remarkable men dispute about some mathematical, scientific, or philosophical subject. Still more interesting was it, however, to watch, when he was present, the incomparable Helmholtz looking silently on, from his calm Olympian heights, with an appreciative but meaning smile as the discussion proceeded."

But although Bunsen was not a mathematician as compared with the men mentioned above, he not only possessed great mathematical ability, but what is more important, the power to apply mathematical treatment to chemical problems. He constantly pressed upon all his pupils the necessity for a chemist of a thorough training in mathematics and physics; indeed, I have heard him exclaim, "Ein Chemiker der kein Physiker ist, ist gar nichts."

Bunsen at the time of his death had been for many years our senior Foreign Member, having been elected on February 1, 1842, during the first session of our Society. It was not till 1858 that he became a Foreign Fellow of the Royal Society. In 1860, the Copley medal was awarded to him, and in 1877 he and Kirchhoff were presented with the Davy medal, being the first occasion of its award, in recognition of their researches and discoveries in spectrum analysis.

With respect to the award of the Davy medal, Bunsen writes to me on Nov. 10, 1877, as follows: "My best thanks for your friendly letter with the news of the very unexpected distinction which has been conferred upon me. I received it almost simultaneously with the official announcement from Williamson, and I am indeed quite confused by so much kindness from my English friends."

Another English honour conferred upon him was that of the award in 1898 of the Albert medal of the Society of Arts given for "distinguished merit in promoting art, manufacture, or commerce," in recognition of his numerous and most valuable applications of chemistry and physics to the arts and to manufactures.

Almost up to the last Bunsen continued to take a vivid interest in the progress of scientific discovery, and though suffering from pain and weakness, ever preserved the equanimity which was one of his lifelong characteristics. Three days before his death, so Quinke writes to me, he lay in a peaceful slumber, his countenance exhibiting the fine intellectual expression of his best and brightest days. Thus passed away, full of days, and full of honours, a man equally beloved for his great qualities of heart as he is honoured for those of his fertile brain, the memory of whom will always remain green amongst all who were fortunate enough to number him amongst their friends.

[Before commencing the Lecture, Sir Henry Roscoe read the following telegram from Dr. Philipp Bunsen of Marburg, the nephew and executor of the late Professor. "On the occasion of the Memorial Lecture, the Bunsen family joins sincerely with the illustrious Society and sends respectful thanks and compliments."]

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# ANNUAL GENERAL MEETING,

MARCH 29TH, 1900.

Professor THORPE, LL.D., F.R.S., President, in the Chair.

I have the pleasure to inform you on this, the 59th Anniversary Meeting, in a phrase which from its constant recurrence may well be stereotyped, that the Society continues to grow and prosper. The number of our Fellows steadily increases year by year, and their communications continue to add, in an increasing degree, to the dignity and usefulness of our organisation. As you will glean from the detailed statement to be submitted by the Treasurer, our financial position is no less satisfactory.

Our numerical position may be stated as follows :

Number of ordinary Fellows on March 29th, 1899 ...	2230
"                    "          reinstated by Council ...	4
"                    "          since elected .....	118
	<hr/>
	2352
Withdrawn .....	20
Removed on account of non-payment of arrears	15
Deceased .....	25
	<hr/>
	60
Number of ordinary Fellows on March 29th, 1900 ...	3292
Number of Foreign Members on March 29th, 1899...	38
Deceased .....	5
	<hr/>
Number of Foreign Members on March 29th, 1900...	33

The names of those who have withdrawn are:—Henry Austin Appleton; Howard Barrett; Claude H. Bater; Richard A. Bush; G. W. Davies; Alfred George Earl; J. M. Fallon; W. A. Greaves; H. Loft Haller; M. Holzmänn; A. Wentworth Jones; John Temple Leon; Prosper H. Marsden; Walter George McMillan; T. Ormerod; J. R. Skelton; Edward Smith; Henry J. Staples; Claude T. Vautin

The names of those removed are:—Eugen Blume; Rev. J. Camp-

bell; J. E. Foakes; Bertram Hunt; H. Hyatt; J. D. Johnstone; C. L. Kennicott; H. A. Lawrance; W. J. Martin; K. P. McElroy; T. G. Nicholson; J. H. Overton; A. E. Potter; John Provis; J. Wrightson.

The names of the deceased Fellows are:—Joshua Buchanan; Kanny Lall Dey; J. B. Edwards; Sir Edward Frankland; William Harkness; John F. Hodges; John Elias Hughes; Eric H. Jackson; Alexander McDougall; W. Marcet; Walter Newton; G. H. Ogston; Robert Oxland; R. T. Plimpton; Henry Charles Reynolds; J. G. F. Richardson; W. H. Richardson; Thomas Glazebrook Rylands; Edward C. Cortis Stanford; Sidney Augustus Sworn; Andrew Taylor; William Thorp; Ferdinand Tiemann; David Watson; W. Lloyd Williams.

Obituary notices of a number of these gentlemen have been supplied to me by the kindness of their friends, and will appear subsequently. The passing away, however, of so eminent a member of our body, and of one who played so leading a part in the development of chemistry, as Sir Edward Frankland, is no ordinary event in the history both of science and of our Society, and demands a special reference. The Council have accordingly determined that Sir Edward Frankland's services to our Society and to science shall be commemorated in the manner hitherto restricted, with the special exception of the case of the late Professor von Hofmann, to our Honorary Foreign Members; and that a Memorial Lecture on the life-work of our former President shall be given in the autumn, and they have requested his pupil, collaborator, and friend, Professor Armstrong, to undertake this duty.

The names of the deceased Foreign Members are:—Robert Wilhelm Bunsen; Charles Friedel; Lars Fredrik Nilson; Carl Friedrich Rammelsberg; and Peter Waage.

Bunsen, who was elected a Foreign Member during the first session of the Society, namely, as far back as February 1st, 1842, and who was long the *doyen* on the list, died on August 16th, 1899, in his 89th year. His friend and former pupil, Sir Henry Roscoe, a past President of the Society, than whom no one is better qualified for such a duty, has undertaken, at the request of the Council, to commemorate the signal services which our illustrious Foreign Member rendered to physical science, and, as the Fellows are already aware, the Memorial Lecture will be given to-night.

Charles Friedel, Member of the Institute and Professor of Chemistry in the Sorbonne, who was elected a Foreign Member of our Society on May 18th, 1876, died on April 20th, 1899, at the age of sixty-seven. His friend and co-worker, Professor J. M. Crafts, of the Massachusetts Institute of Technology, and a Fellow of this



Society, has kindly responded to the invitation of the Council to prepare a Memorial Lecture on our deceased colleague, and in a letter just received from him he holds out the hope that he may be able to deliver it in person on some day in the latter half of June next.

Lars Fredrik Nilson, Professor of Agricultural Chemistry in the Kongl. Landtbruks-Akademien, Stockholm, and formerly Professor of Analytical Chemistry in the University of Upsala, whose name is specially connected with the chemistry of the so-called rare earths, and who was elected a Foreign Member of this Society on February 2nd, 1888, died on May 14th, 1899, in his 59th year. Professor Otto Pettersson, of the Free University of Stockholm, who was associated with Nilson in much of his work in pure chemistry, has undertaken, in compliance with the wish of the Council, to give the Society an account of the many services which his friend rendered to chemistry, and he hopes to be able to visit London for this purpose in the first week of July next.

Carl Friedrich Rammelsberg, Geh. Reg.-Rath., and Emeritus Professor of Inorganic Chemistry in the University of Berlin, who was elected a Foreign Member of this Society on May 3rd, 1866, died on December 28th, 1899, in his 87th year. Professor H. A. Miers, of Magdalen College, Oxford, and a Fellow of this Society, has kindly acceded to the wish of the Council to prepare a Memorial Lecture on the lifework of the veteran mineralogical chemist, who was born only a year or two after Wollaston, first described the reflecting goniometer, and of which no one has made a greater use than our deceased colleague. Professor Miers hopes to be able to deliver his Lecture to the Society in December next.

Peter Waage, Professor of Chemistry in the University of Christiania, and whose name is known to all here in connection with his studies in chemical affinity, made in association with his colleague Professor Guldberg, died on January 13th of this year. He was elected a Foreign Member of our Society on January 20th, 1898. Our Vice-President, Professor Ramsay, has kindly supplied an account of his work, which will be found among the obituary notices.

Since the last Anniversary, 175 communications have been made to the Society, a number greater than in any preceding year. In character, variety, and importance, they compare not unfavourably with the contributions of any former period. Abstracts of all of these have appeared in the Proceedings, and 83 have already been published in the Transactions. The volume of Transactions for 1899 contains 120 memoirs, occupying 1166 pages; in the preceding year 102 papers were published, occupying 1038 pages.

The increasing mass of literature thus to be dealt with is a matter of much concern to the Publication Committee, and our annual volume

threatens to assume unwieldy proportions. Authors for the most part show a praiseworthy desire to express themselves as concisely as possible. At the same time, there is occasional room for improvement in this respect, and one of the most difficult and invidious tasks of a long-suffering Editor is to induce contributors to effect such a degree of condensation as will enhance the strength and quality of their communications. I may also be pardoned for pointing out that much trouble and expense would be saved to the Society if authors would cause their communications to be type-written, or at least fair-copied, and the accompanying illustrations to be so prepared as to obviate the necessity of redrawing them for "process" reproduction. I may further hint that it would conduce to uniformity, and not unfrequently to intelligibility, if authors would conform, as far as practicable, to the system of nomenclature and notation prescribed for use in the Abstracts. This system has recently been fully reconsidered by the Publication Committee with the friendly co-operation of a large number of the more active workers of the Society, and the revised Regulations will appear in the forthcoming Supplementary Number. The Editor is, I am sure, always ready to consider the sensitive feelings of the "conscientious objector"; but there are latitudinarians in chemistry as in other spheres of intellectual activity, and to such a word in season may not come amiss.

The volumes for 1899 contain 3,617 Abstracts of papers published mainly in Continental journals, occupying 1,796 pages, arranged as follows:

PART I.		
	Pages.	No. of Abstracts.
Organic Chemistry .....	968	1477
PART II.		
General and Physical Chemistry .....		421
Inorganic Chemistry .....		417
Mineralogical Chemistry ... ..		211
Physiological Chemistry .....		236
Chemistry of Vegetable Physiology and Agriculture .....		244
Analytical Chemistry .....		611
	828	2140
Total in Parts I. and II. ....	1796	3617

The number of papers dealt with in 1899 is 791 more than in the preceding year. I am pleased to be able to state that all arrears in

abstracting have at length been overtaken. The Fellows may now count upon having the monthly *résumé* of contemporary chemical literature brought to their attention as quickly as it is possible to furnish it.

It will have been observed also that the Editor has succeeded in issuing the Journal somewhat earlier in the month than has hitherto been thought possible.

The question of co-operation with other English-speaking Chemical Societies in the preparation of abstracts of foreign chemical literature was referred to in the last Presidential Address. But, although the matter has been considered, the Committee appointed to deal with this question has not yet reported. The subject is surrounded with considerable difficulties: in the words of my predecessor, "It would be unwise to ignore the grave consequences to the financial position of the Society which might result from any too precipitate change in the method of publication of the Abstracts."

637 copies of the 1883—92 Index and 317 of the 1873—82 Index were issued to Foreign Members, Institutions, and to those Fellows who, being entitled to a free grant of them, had made application within the prescribed period. 565 of these applications had been received, of which 43 were those of Fellows resident abroad.

The work of compilation of the Collective Index showed the necessity of indexing the annual volumes in a more systematic and consistent manner than had been done in the past. For the last four years, the work of indexing the annual volumes has been done by a special staff of indexers under the direction of the Sub-Editor. This plan has worked well as regards uniformity and consistency, but, unfortunately, it has not been possible, by means of it, to bring out the Annual Index with that promptitude which is desirable. The Index Committee has, therefore, suggested to the Council the propriety of entrusting the work of indexing to one person to be responsible, under the direction of the Editor, for the preparation and speedy publication of the work. The Council has adopted the suggestion, and sanctioned the employment, on this work, of Mrs. Dougal, who is already favourably known to the Fellows for the excellent service she rendered the Society in editing the Collective Indexes of its publications since 1873.

The Fellows are doubtless aware the Society stocks a certain number of its publications, and the question of the custody and supply of back numbers has received attention. During the recess, the room in which these are stored has been rearranged and made more convenient of access. As will have been gathered from a special notice issued with the Proceedings, a limited number of sets of the Memoirs and Proceedings of 1841—7, of the Quarterly Journal 1849—62, and of the First Series of the Journal from 1863 onwards are now on sale.

I am glad to be able to report that the Fellows show an increasing

desire to use the library, 790 books having been borrowed as against 727 last year. Under the *régime* of a more generously disposed Treasurer, there has been a considerable addition of books, periodicals, and pamphlets to the library, namely, 114 books, 397 volumes of periodicals, and 27 pamphlets, as against 67 books, 285 volumes of periodicals, and 24 pamphlets last year. I can only express a hope that during this period of acute depression in the publishing world the quality of the added literature is at least commensurate with the increase in its quantity.

The condition of the Library Catalogue has long required attention, and my predecessor in his Address last year made reference to the desirability of revising it. There have been five catalogues since the library was founded in 1850, namely, the first in 1851, the second in 1861, the third in 1869, the fourth in 1874, and the fifth in 1886. The Council has directed a new catalogue to be prepared according to a scheme drawn up by the Library Committee, and the work is well advanced under the direction of Mr. Steele, assisted by Miss Morfee.

Three meetings of the Research Fund Committee have been held during the last twelve months, and grants amounting to £192 have been made in aid of chemical investigation. We are now beginning to feel the benefit of Mr. Tustin's generosity in the increased sum at our disposal for distribution. This year it falls to my happy lot to award the medal which is associated with the name of one of the most munificent patrons of the Research Fund. On the unanimous recommendation of the Committee, adopted with equal unanimity by the Council, it has been decided to award the Longstaff Medal to Dr. W. H. Perkin, junior, F.R.S., Professor of Organic Chemistry in the Owens College, Manchester, whose name worthily follows, after an interval of twelve years, that of Dr. W. H. Perkin, senior, on the list of the recipients of the highest award which it is in the power of the Society to bestow on its Fellows.

Dr. PERKIN, it gives me a special pleasure to ask you, on behalf of the Chemical Society, to transmit this medal to your son, Professor W. H. Perkin, who, to our great regret, is unable to be here to receive it in person. The Longstaff Medal has been awarded to him for his researches on closed chain compounds of the trimethylene and similar series, and for his recent important syntheses of camphor derivatives.

The Council desire, in making this award, to indicate how highly they regard the contributions with which he has enriched our Transactions. Under his stimulating influence, the chemical laboratory of the Owens College, and especially that section of it under his more immediate direction, continues, as of old, to furnish a succession of valuable memoirs to English chemical

literature. They trust that this activity may long be maintained, and that our Society may continue, as in the past, to enjoy the credit and distinction of disseminating the results of the inquiries to which his fruitful ideas give rise.

During the long vacation, the building has been thoroughly cleaned and redecorated, and by the kindness of the Office of Works certain much needed improvements in our lavatory accommodation and in the sanitary arrangements of the building have been effected.

The accommodation at the disposal of the Society is, however, a matter of growing concern. Our Meeting Room seats no more than 157 persons in spite of the increased space which was gained as the results of the alterations in 1892. This is altogether incommensurate with our present numerical strength, and, as the Fellows well know, considerable inconvenience is occasionally felt owing to the impossibility of finding room for those who wish to attend the meetings. Our collection of books is gradually overspreading into every room we possess, and such conveniences as we have for the discharge of our official business and for the custody of our official records are greatly curtailed by the increasing inadequacy of our space.

We are indebted to several of our Fellows for additions to the artistic possessions of the Society. Dr. Debus has presented us with a striking bust of Humphry Davy, a cast of one modelled during his lifetime by Miss Moore. In accordance with the donor's wishes, this bust now appears in our Meeting Room. On the recommendation of Mr. Thomas Armstrong, C.B., formerly the Art Director of the Science and Art Department, who was much impressed with the artistic quality of Miss Moore's work, this bust has been copied by Miss Levick, with certain adaptations taken from Sir Thomas Lawrence's well-known portrait in the possession of the Royal Society, and has been reproduced in bronze. The reproduction, together with its pedestal, has been given by our colleague, Dr. Messel. We also owe to the kindness of Dr. Atkinson a medallion of Wöhler executed in electrotype by our former President, Dr. Hugo Müller. Sir Henry Roscoe has given to us some interesting mementos of his association with the great man whose scientific labour he is to commemorate to-night.

The Society has had the agreeable duty of congratulating Sir George Gabriel Stokes on his Jubilee as Lucasian Professor of mathematics in the University of Cambridge, and I was deputed by the Council to prepare and present an address, of which the text has already appeared in the Proceedings. In acknowledgment, the University of Cambridge has forwarded to the Society a copy of the medal, bearing a portrait

of Sir George Stokes, which was struck in commemoration of this happy event.

We have also had the pleasure of felicitating two of the most eminent of our Foreign Members on the attainment of the 25th anniversary of their doctorate, namely, Professor Emil Fischer, and Professor van't Hoff, both of the University of Berlin.

Although Century-summaries run a risk of being regarded as flat, stale, and unprofitable, I have ventured to think that it would not be uninteresting or altogether unuseful if, at this time, I sought to indicate in the broadest possible outline what our countrymen have done during the past hundred years in gaining and extending knowledge within the special province of intellectual activity with which we, as a Society, primarily concern ourselves.

In examining the century's accounts, we naturally inquire into the nature of the balance with which it started. How much better it was felt to be than at the corresponding period of the eighteenth century may be gleaned from the circumstance that the Council of the Royal Society—actually the contemporaries of Newton—entered upon 1701 with the complaint, more petulant than dignified, that “the discouraging neglect of the great, the impetuous contradiction of the ignorant, and the reproaches of the unreasonable, had unhappily thwarted them in their design to perpetuate a succession of useful inventions.” During the years that followed, the achievements of Newton's successors, Franklin, Dollond, Maskelyne, Canton, Priestley, Hunter, made the Fellows feel that they were not wholly dependent upon the patronage of the great, although, as the battle over the lightning conductors too plainly showed, they were not altogether unmindful of the frowns and reproaches of the ignorant and unreasonable.

Let us then try to realise what was the state of things, so far as it may be thought to affect Chemistry and its pursuit, in the year 1800. To begin with, the population of these isles was less than half of what it now is. London contained only about 800,000 persons, and I need hardly say that the whole social and economic conditions of the people were vastly different from what they are to-day. In one respect, at least, the circumstances of this and that time were alike—we were at war. But the condition of the nation now is halcyon compared with what it was in 1800. England was then in such straits as she never was before. Her very existence as a nation was at stake. The harvest over a great part of the country had failed. Corn was upwards of £9 a quarter, and famine and pestilence brooded over the land. Whilst Napoleon's attempt at invasion had roused the nation to a defiant and stubborn resistance, the governing classes were torn

asunder by party faction and seemingly more eager to secure political supremacy than to devise means to resist the common enemy.

Under such untoward conditions, it might well be supposed that science would languish and decay. Such, however, was not the case. It is a singular fact, and the circumstance is not peculiar to our own history, that it is precisely during the lean years—during periods of national stress and strain—that some of our greatest intellectual triumphs have been won. In the history of Science, and especially of Chemistry, France was never more glorious than during the turmoil which preceded and followed the Reign of Terror, and in our own case never were such chemical triumphs achieved as during the gloomy period covering the dying years of the last century and the opening years of that which is now drawing to its close.

What, then, was the condition of chemical science in Great Britain in the year 1800? Who were its cultivators and what were they doing? Black had died in the preceding November; Priestley, who had suffered "the slings and arrows of outrageous fortune" in vainly buffeting with the times, had been settled some six years on the banks of the Susquehanna, occupying himself with his beloved theology and in futile efforts to resuscitate the dying doctrine of phlogiston. For, in 1800, phlogistonism had only been scotched in this country. Mr. Richard Kirwan, President of the Royal Irish Academy and Inspector-General of his Majesty's Mines in the Kingdom of Ireland, had, it is true, some years previously tried conclusions with the French chemists in his *Essay on Phlogiston*, which had been translated by Mme. Lavoisier, in order to be refuted, point by point, by Lavoisier, Morveau, Laplace, Monge, Berthollet and Fourcroy. The new theory was, in fact, indebted to this opposition for some of the strongest proofs on which it is founded. The nimble-witted Irishman found he was no match for this formidable battalion. He confessed himself vanquished, and, as he wrote to Berthollet, laid down his arms. Rather, he might have said, he went over to the enemy, for during the few years of activity which remained to him he preached the new doctrine with all the zeal of the convert, albeit a little restive at times under the tyranny of the nomenclature it imposed upon the chemical world. National prejudice, and the authority of Priestley and Cavendish no doubt retarded its general adoption in this country. Cavendish, at the close of the last century, was in his 69th year; he had ceased to engage in chemical inquiry, although still keenly interested in its progress. James Watt, who played so notable a part in the events which led to the discovery of the composition of water, and younger by some five years than his quondam rival, was no longer actively occupied with chemical speculation. Wollaston, as dispassionate and hardly less reserved than Cavendish, was in his 34th

year, struggling to get together the medical practice which his singularly cold and taciturn manner forbade him to expect. John Dalton, also in his 34th year, had just resigned his post as tutor at the Manchester Academy, where, as the Trustees were pleased to report, "he had uniformly acquitted himself to their entire satisfaction in the province of mathematics, natural philosophy, and chemistry," on the spacious salary of £80 a year, and was now looking out for pupils in those branches of learning at the rate of two shillings a lesson. Thomas Thomson was 27; Andrew Ure, of dictionary fame, was 22—the same age as Humphry Davy, who was still at the Bristol Pneumatic Institute, where he had published his "Researches, Chemical and Philosophical, chiefly concerning Nitrous Oxide." William Thomas Brande was a lad of 12; and little Michael Faraday, a child of 8, who lived in a mews near Manchester Square, keeping body and soul together on the weekly loaf he got from public charity and whiling away his leisure in playing marbles in Spanish Place.

Of course, the results of the more important chemical investigations of the period were laid before the Royal Society, and were published in the *Philosophical Transactions*, and subsequently in *Nicholson's Journal* or *Tilloch's Philosophical Magazine*. The Society at that time was, and had been for the previous 22 years, under the benevolent despotism of Sir Joseph Banks. The other officers were Wegg, Planta, Gray, and Layard. The meetings were held in the evening at 8 o'clock, and, of course, for the most part by candle-light, in one of the large rooms in Somerset House, or Somerset Place as it was then termed. The Society had moved, in 1780, from Crane Court into apartments provided for them by the munificence of their patron, George III., and the skill of his architect, Sir William Chambers, which habitation, in the language of the Council, "it was hoped would confer on them an external splendour in some measure proportional to the consideration in which they had been held for more than a century." Hard by was the Crown and Anchor Tavern, where the Royal Society Club held its pious orgies; the expense of the dinner was limited to five shillings, and black puddings were a standing dish. It is evident that the drowsy philosophers did no violence to their digestion by a too prolonged attention to the intellectual fare of the evening, for even a comparatively short communication not unfrequently occupied two if not three sittings. The President, when in town, lived in the then fashionable neighbourhood of Soho Square. Cavendish's town house was at the corner of Montague Place and Gower Street, and from here he might be descried, in a faded violet court dress, frilled shirt front and wrists, with a great-coat of greyish-green, and a three-cornered cocked hat over his knocker-tailed periwig, slouching along,



one hand behind his back, on the way to his library in Dean Street, Soho. Wollaston lived in Hunter Street, Brunswick Square, and subsequently in Dorset Street, Manchester Square; Smithson Tennant oscillated between his farm at Cheddar and his chambers in the Temple; and Charles Hatchett resided in the rural district of Hammersmith. Other notable chemical workers at this period were William Henry, of Manchester, William Haseldine Pepys, and Richard Chenevix.

There were, of course, other publishing agencies at work, with aims similar to those of the Royal Society, such as the Royal Society of Edinburgh, which grew out of a Society founded in 1731 by the leading medical men of that city; and the Royal Irish Academy, founded in 1782, and of which Kirwan was President for some years. Many of the provincial towns, too, had their Literary and Philosophical Societies, but with the exception of that at Manchester, to which the Henrys and Dalton were frequent contributors, their Proceedings and Transactions contain few important chemical memoirs during the first years of the century.

Theoretical chemistry was taught in the Universities, and in some of them, following the example set by Black, by means of experimental courses of lectures. At Oxford, there had been Beddoes, but his political opinions were distasteful to the University, and he had resigned. At Cambridge, there were F. J. Wollaston and Farish. Hope, who first made known the existence of strontia, lectured at Edinburgh; Robert Cleghorn at Glasgow; and Dr. French, who is credited with the saying that "Humphry Davy was a verri troublesome person in chemistry," taught at Aberdeen. Moreover, almost every large town had one or more teachers—men of the type of Varley, Garnett, and Aikin—who gave lessons at their private houses. Faraday relates how, during his bookbinding days, his master allowed him to go occasionally of an evening to hear the lectures delivered by Mr. Tatum, at his house in Dorset Street, of which he obtained knowledge by bills in the streets and shop windows. The hour was eight o'clock in the evening, and the charge was one shilling. More ambitious or more self-important people than Mr. Tatum announced their prospective courses among the *Miscellanea* of of Tilloch's or Nicholson's Magazines. Thus, Dr. Beddoes informs the world that his "Lectures are to be calculated for both sexes and different ages; and that there may be little chance of exclusion by reason of narrow circumstances, the subscription is fixed at one guinea; but unless fifty persons shall have entered their names by the 31st of March, the Lectures will not go on, as without a tolerably numerous audience, Dr. B. thinks he could bestow his time in a manner more advantageous to the public."

The principal manuals of the time were Kerr's translation of Lavoisier's "Elements"; Chaptal's "Elements," the standard text-book on applied chemistry; Parkinson's "Chemical Pocket-book or Memoranda Chemica"; Heron's "Elements"; Brisson's "Physical Principles of Chemistry"; Accum's "System of Theoretical and Practical Chemistry"; and Marcet's "Conversations."

The first two decades of this century are unquestionably the most momentous and the most brilliant of any period in the history of chemistry in our country. They witnessed the establishment of the fundamental laws of chemical combination and the atomic theory; the discovery of the so-called gaseous laws and of the real nature of the atmosphere; the application of voltaic electricity as an analytic agent; the isolation of the metals of the alkalis and of the alkaline earths; the determination of the chemical nature of the halogens; and in the discovery of tantalum, palladium, iridium, osmium, and rhodium a considerable addition to the list of the metallic elements. These, in 1802, were only 23 in number, as against about 60 at the present time.

A number of new compounds were brought to light or identified during the same period—such as fulminating mercury and fulminating silver, carbonic oxide, acetylene, phosgene gas—for the most part substances deemed at the time of their discovery to be merely chemical curiosities, incapable from their very nature of being turned to useful account, but all of which are now of important practical application. The same period witnessed the invention of the reflecting goniometer and of the miner's safety lamp. It saw the establishment of gas lighting, and with it the creation of an industry which has exercised a profound effect on the development of the chemical arts. It saw, too, the first attempt to control, by the aid of chemical analysis, the hygienic character of the drinking water supplied to a large community. The statement, in 1808, of Dr. Andrew Ure, who became Professor of Chemistry in Anderson's College in 1818, that the water from the wells in Glasgow, which were then the chief sources of supply, contained "a surprising quantity of heterogeneous matters in solution," paved the way for the action of Telford and Robertson Buchanan in bringing in "the inexhaustible supply from the river Clyde by means of pipes and steam engines." In the *Philosophical Magazine* for 1808 we read that this was the first occasion on which the whole of a public supply was filtered "by means of reservoirs constructed for the purpose. . . . This salutary process is effected by making the water filter through sand and gravel from the large reservoir into which it is first elevated by the steam engine into a second reservoir posited a little lower and from which the conveying-pipes receive their supply." It is not often that Glasgow i

willing to take a lesson from Paisley, but it is interesting to read that a Paisley 'buddy' first practised the filtration of water intended for public supply, and it is satisfactory to learn further that "this public spirited adventurer was amply remunerated for his expenditure."

The promulgation of the atomic theory and the importation of the ideas of constancy of chemical composition and of definite numerical ratio gave an immediate impetus to analytical chemistry, of which the operations were at length seen to be subject to a numerical check and control hitherto unknown and barely suspected. Whilst the reflecting goniometer, on the one hand, served to define the geometrical form of a substance and to establish the constancy of that form with a precision unattainable by the graphometer of Carangeau, the balance, on the other, rendered more and more perfect, in response to the demands of the chemist upon the mechanician, in order to satisfy the conditions imposed by the fundamental laws of Dalton's hypothesis, served to determine its exact atomic composition. The first use to which Wollaston, in 1810, put his reflecting goniometer was to measure with exactitude the primary angles of calcspar, the composition of which had been accurately ascertained by Richard Phillips in 1803. A number of compounds indeed had their real nature and composition established during this period, and in the light of the atomic theory. In fact, the memoir by Thomson on the Oxalates (*Phil. Trans.*, 1808), and that by Wollaston "On super-acid and sub-acid Salts" (*Phil. Trans.*, 1808), were of the greatest service as proving the validity of Dalton's theory of chemical combination. Smithson Tennant analysed emery; Hatchett ascertained the composition of magnetic pyrites; Chenevix that of the arseniates of copper and iron, and of bournonite; Thomson that of sodalite, fluorspar, and allanite.\* Edward Clarke, of Cambridge, analysed petalite, gehlenite, the purple of Cassius, and examined the newly-discovered metal cadmium and its salts.

It would be impossible to exaggerate the influence which the discoveries of the first twenty years of the century exerted on the spirit of the age. They seemed, indeed, to presage a new era—the coming of a glorious day of which the dawn had already begun. No generalisation was more opportune in its announcement than that of Dalton; it was indeed, to use the common phrase, "in the air"; the teaching of a long succession of philosophers and the experimental labours of many workers had paved the way for its acceptance, and it is practically certain that had Dalton not formulated it Wollaston or Berzelius would have done so. As it was, each of these distinguished men was almost immediately able to supply the strongest experimental proof of its soundness. Wollaston, from the outset, was well

\* Allanite, in addition to cerium, contained, as he supposed, a new metal which he proposed to distinguish by the name of "junonium."

aware of the limitations of Dalton's explanation of the facts of chemical combination ; and he recognised that the arithmetical relation alone of the proportions of elementary atoms is insufficient to explain their mutual action. As he says, "we shall be obliged to acquire a geometrical conception of their relative arrangement in all the three dimensions of solid extension." How Berzelius received the news of Dalton's discovery he has himself related in his memorable paper in Gilbert's Journal. This view of the combinations of bodies, he says, "appeared capable of illustrating so greatly the doctrine of affinity, that the confirmation of Dalton's hypothesis seemed to be the greatest step that chemistry, as a science, would have made during the whole time of its existence." How it was confirmed by Berzelius it is not necessary here to state, nor need we set out in detail how the whole course of modern chemistry, however complex and many-sided it may seem, is really one vast elaboration of the atomic theory : in fact, as Liebig has said, all our ideas are so interwoven with that theory that it is difficult to carry ourselves back to the time when it did not exist. Dalton was the first recipient of one of the Royal medals which the Sovereign, on the recommendation of the Royal Society, annually bestows, and no more just award was ever made. Davy, in making known, as he said, "this first testimony of royal benevolence to science," stated that this discovery of the simple principle, universally applicable to the facts of chemistry, laid the foundations for future labours respecting the sublime and transcendental parts of the science of corpuscular motion. Dalton's merit, in this respect, resembles that of Kepler in astronomy. "The causes of chemical change are as yet unknown, and the laws by which they are governed ; but in their connection with electrical and magnetic phenomena, there is a gleam of light pointing to a new dawn in science ; and may we not hope that in another century, chemistry having, as it were, passed under the dominion of the mathematical sciences, may find some happy genius, similar in intellectual powers to the highest and immortal ornament of this Society, capable of unfolding its wonderful and mysterious laws."

Volta's famous letter of March 20th, 1800, to Sir Joseph Banks, was as the 'order of the day' of a great leader. No more momentous document was ever given to the scientific world. "The voltaic battery," said Davy, in one of his characteristically happy phrases, "was as an alarm-bell to experimenters in every part of Europe ; and it served no less for demonstrating new properties in electricity, and for establishing the laws of this science, than as an instrument of discovery in other branches of knowledge ; exhibiting relations between subjects before apparently without connection, and serving as a bond of unity between chemical and physical philosophy."

It is not necessary here to dilate upon what this "instrument of

discovery" in the hands of our countrymen has done for the development of chemistry. April 30th, 1800, when Nicholson and Carlisle first effected the decomposition of water by electrolysis, is a red-letter day in the history of our science. The *Transactions of the Royal Society*, *Nicholson's Journal*, and the *Philosophical Magazine* in the first years of the century show with what ardour and with what a lively expectancy "the new galvanic apparatus of Mr. Volta" was applied.\*

Although even as far into the century as the date of Waterloo, the theory of the compound nature of water was regarded by some as "nothing more than a fanciful conjecture" and "a bare assertion without any proof whatever," there can be no question that Nicholson and Carlisle's discovery was of the greatest service in affording what was then, and long subsequently, looked upon as one of the strongest analytical proofs of the validity of the fact. But in their effect upon the popular imagination, these discoveries altogether paled before that of Davy. The isolation of potassium is, in reality, one of the most dramatic episodes of an epoch fruitful in striking incidents. The remarkable nature of the substance itself, its intense chemical activity, its significant chemical relationships, and the astonishing and far reaching possibilities which its very existence seemed to open out, were all calculated to impress the minds of *virtuosi* and vulgar alike. Davy's triumph, indeed, was regarded as the realisation of a confident anticipation that the most important discoveries in chemistry were about to be made by the help of galvanism—an anticipation which found expression in almost every issue of the scientific journals of the time. There is little wonder, therefore, that a succession of scientific events of such magnitude as those which characterised the opening years of this century should have powerfully excited the imaginations of all cultured persons, and that optimists in every country, under the sway of ideas which made up the social and political philosophy of the time, should look forward in sure and certain hope to the immediate advent of a new era—to the coming of a regenerated humanity in a golden age. Thus Christopher Girtanner, of Göttingen, whose name lives only in connection with the fact that he was the first German chemist to appreciate and teach the new doctrines of the French School, was convinced that in the 19th century the transmutation of the metals would be generally known and practised. "Every chemist," he says, "every artist, will make gold; kitchen utensils will be of silver, and even gold . . . There will be no other riches than natural riches—the productions of the soil; artificial riches,

\* This at the time was usually constructed of plates of silver and zinc, with intervening pieces of cloth. "Most of our philosophers," we are told, "have used half-crowns for the silver plates," and zinc could be bought at 8d. per lb. at the White Lion in Foster Lane, and cast in moulds of chalk.

such as gold, silver, and paper money, will vanish in the hands of those who have accumulated them. What a revolution in society! Every enlightened chemist, however, will agree with me that this revolution is not only probable, but at no great distance." Unhappily for Dr. Girtanner's reputation as a prophet, the social revolution he foretold may not be reckoned among the achievements of the 19th century. Enlightened chemists still appear to have an eye to artificial riches, not scorning even paper money; and although, unfortunately, the precious metals do occasionally vanish in our hands, it is not because we convert them into kitchen utensils.

Even the sober-minded Faraday was not insensible to the visions thus created. In the course of his lectures on the metals, given in 1818 to the City Philosophical Society, he says, "to decompose the metals, then to reform them, to change them from one to another, and to realise the once absurd notion of transmutation, are the problems now given to the chemist for solution. Let none start at the difficult task, and think the means far beyond them. Let us but look to the means which have given us these bodies, and to their gradual development, and we shall then gain confidence to hope for new and effective powers for their removal from the elementary ranks. . . . Consider the improvement when, by a variety of manipulations, the early chemist of the last century separated a small quantity of a metallic substance from five or six other bodies, where it existed in strong combination, and then passed to the perfection of these means as exhibited in the admirable researches of Tennant and Wollaston; lastly, glance but at the new, the extraordinary powers which the chemist of our own nation put in action so successfully for the reduction of the alkalis and earths, and you will then no longer doubt that powers still progressive and advanced may exist and put at some favourable moment the bases of the metals in our hands."

It is interesting to note that even as far back as 1806 an effort was made to form a Chemical Society independent of the Royal Society, to be called the London Chemical Society, but it received scant encouragement from persons in high places, and few chemists of note joined its ranks. Sir Joseph Banks, indeed, frowned down upon all such attempts. "I see plainly," he once said, "that all these new-fangled associations will finally dismantle the Royal Society, and not leave the old lady a rag to cover her." And the frown of the masterful old President meant social ostracism to all who chose to disregard it. But, unlike his predecessor, Sir John Pringle, who, on a certain memorable occasion, confessed to George III. that he was unable to reverse the laws and operations of nature, and was then told he had better resign, Banks, if he could not reverse, could at least control and modify a natural tendency, and with the aid of

Wollaston, Davy, Hatchett, and Brande he managed to keep chemistry for a time almost exclusively under the cloak of "the old lady."

Priestley died on February 9th, 1804. Although he lived long enough to have read of Dalton's explanation of the laws of chemical combination, as explained in Thomson's "System," and although he must have heard of the electrolytic decomposition of water by Nicholson and Carlisle in 1800, nothing apparently could shake his conviction of the essential and inherent truth of the conception of phlogiston. The last of his published writings was his memoir on "The Doctrine of Phlogiston established, and that of the Composition of Water refuted." Tolerant and receptive as he was in all other matters of opinion, and especially in matters of religious belief, he seemed utterly incapable of appreciating the real significance of the rapidly accumulating mass of facts, or of drawing any correct inferences from them.

Cavendish, "le plus riche de tous les savans et probablement aussi le plus savant de tous les riches," died in 1810. His work belongs to a preceding age, for on the downfall of phlogistonism he had ceased to occupy himself with chemical pursuits, and it must ever remain doubtful how far he gave in his adhesion to the new doctrine to which his own cardinal discovery so largely contributed.

In the year 1815 appeared in Thomson's *Annals of Philosophy* (3, 321) an anonymous essay "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms," which the author states he submits "to the public with the greatest diffidence; for, although he has taken the utmost pains to arrive at the truth, yet he has not that confidence in his abilities as an experimentalist as to induce him to dictate to others far superior to himself in chemical acquirements and fame." With this modest preamble the author proceeds to discuss certain consequences which seem to him to follow from the doctrine of volumes as first generalised by Gay Lussac. The paper is remarkable, in spite of its errors and crudities, for its originality and lucidity. Its author was eventually discovered to be William Prout, then a young medical student, who lived to become eminent as a physiological chemist. His work thus tentatively put forward has become classical as containing or, rather, suggesting, the hypothesis that the atomic weights of the elements are multiples of that of hydrogen. For it is noteworthy that the paper nowhere contains in explicit terms the statement of what is now known as Prout's law. Its main purpose was to set out more clearly than had hitherto been perceived the relation between the doctrine of gaseous volumes and of atoms, and it is only incidentally remarked that he "had often observed the near approach to round numbers of many of the weights of the atoms," and that "Dr. Thomson appears also to have made the same remark." He further points out that it

would appear from his tables "that all elementary numbers, hydrogen being considered as 1, are divisible by 4, except carbon, azote, and barytium, and these are divisible by 2, appearing, therefore, to indicate that they are modified by a higher number than that of unity or hydrogen. Is the other number 16 or oxygen? And are all substances compounded of these two elements?" Prout's 'law' has been frequently so stated as to imply that all substances are 'compounded' of hydrogen. But, as will be seen, his own words convey no such idea.

It is not improbable that the idea that all atomic weights were actually integers would have attracted little, if any, attention, had it not been adopted by Thomson and given currency by means of his "System of Chemistry," then, and for some years subsequently, one of the leading British text-books.

Smithson Tennant, Professor of Chemistry in the University of Cambridge, a man of whom it was said, in Johnson's well known words, is "to be mentioned with reverence rather for the possession than the exertion of uncommon abilities," died in 1815—accidentally killed whilst riding in the neighbourhood of Boulogne. Born at Selby in 1761, and a pupil of Black, he was early attracted to the study of chemistry, which he continued to prosecute at Cambridge as a Fellow Commoner of Christ's College. His private fortune exempted him from the necessity of following actively any profession. Although a man of wide reading, and of a quick and active mind, we are told that there was a singular air of carelessness and indifference in his habits and mode of life, his manners, appearance, and conversation being the most remote from those of a professed student. "His college rooms exhibited a strange, disorderly appearance of books, papers, and implements of chemistry, piled up in heaps, or thrown in confusion together." He was fond of foreign travel, and, in the course of one of his journeys, made the acquaintance of Scheele, for whom he had a high admiration. He was also on terms of friendship with many of the leading French chemists of his time. Chemistry in Germany at this period was a mixture of science and credulity, the philosopher's stone was spoken of with respect, and Tennant relates that he received from a man of science and character an introduction to a person who was reputed to be in possession of that treasure, with whom he conversed in Latin, and who exhibited to him the mysterious powder, "enlarging upon its transcendent qualities with much pomp, and in flowing and sonorous periods."

Tennant is best known for his analysis of carbon dioxide, his work on the nature of the diamond, and on the injurious effects of magnesia in agriculture, his chemical examination of emery, and his



discovery of iridium—so-named from the various colours of its solutions, and osmium—which owes its name to the smell of certain of its oxides. In the course of an inquiry by a Committee of the Royal Society, formed at the request of the Government to investigate the danger that might attend the general introduction of gas lighting in the metropolis, he made the observation that flame will not pass through small tubes, a discovery which in the hands of Davy led to the invention of the safety lamp.

The third decade of the century saw the rise of Faraday, Graham, and Edward Turner. Faraday had thrown up book-binding in 1813, and attached himself to the Royal Institution, getting his "baptism of fire" in working upon Dulong's newly-discovered nitrogen chloride, which was then occupying Davy's attention. He assisted Davy, too, in his work on iodine, on the torpedo, on the nature of the diamond, on euchlorine and on the chlorides of phosphorus, and in his memoir on "Some combinations of Phosphorus" the master pays a well-merited tribute to the "accuracy and steadiness of manipulation of his assistant."

Although Davy had propounded his proofs of the elementary nature of chlorine as far back as 1810, and although these had been strengthened by his work on iodine in 1814, his doctrine was not universally accepted, the Scotch teachers in particular, notably Murray and Ure, even as late as 1818, making repeated and determined attempts to subvert it. Faraday did yeoman service in repelling the attack, which eventually degenerated into a wordy warfare between Murray and John Davy.

With the beginning of 1820, Faraday may be said to have served his apprenticeship to science. He had already contributed some two score notices and papers to the *Quarterly Journal of Science*, and had published his remarkable work with Stodart, a surgical instrument maker, on wootz and other alloys of steel. He had discovered tetrachlorethylene, perchlorethane and ethylene diiodide, an account of which constitutes his first paper in the *Philosophical Transactions*, and shortly afterwards he described, with Richard Phillips, a new compound of chlorine and carbon, first observed by Julien, of Abo, and now known as hexachlorobenzene. In 1823 appeared his memorable paper "On fluid chlorine," and immediately afterwards were liquefied hydrogen chloride, sulphur dioxide, carbon dioxide, sulphuretted hydrogen, euchlorine, and nitrous oxide. It should be stated, however, that Monge and Clouet had already condensed sulphur dioxide, probably before the year 1800, and that Northmore, with the assistance of Accum, had obtained liquid chlorine in 1806 by compression at ordinary temperatures (*Nicholson's Journal*, 12 and 13). Northmore's description of the properties of liquid chlorine is so explicit that it is

remarkable that the significance of his observation should have escaped notice. The name and fame of the Royal Institution are indissolubly connected with the work so auspiciously begun by Faraday, and with the liquefaction and solidification of air and hydrogen by my predecessor in this chair this chapter in the history of physical science closes with the closing years of the century. It will ever be accounted among the triumphs of the 19th century that it has effected the removal of those artificial boundaries—the hard and fast lines of demarcation—implied by terms which have now no other rational meaning than as denoting states of physical aggregation. Nor will it be forgotten that it is largely to the labours of our countrymen, Dalton, Faraday, Andrews, and Dewar, that this achievement is to be ascribed.

In 1825, Faraday discovered benzene. He found it among the products furnished by the operations of the Portable Gas Company. Although he ascertained that the density of its vapour was 39, hydrogen being 1, the significance of that circumstance was not perceived at the time. The work of Ampère and Gay Lussac, in fact, was not really understood or appreciated at this period, and the conception of Avogadro lay dormant. "With regard to the composition of this substance," wrote Faraday, "my experiments tend to prove it a binary compound of carbon and hydrogen, two proportionals of the former element being united to one of the latter." What Faraday's bicarburet of hydrogen has developed into need not now be told. The work which has accumulated round this single substance during the seventy-five years which have elapsed since it has been known constitutes one of the most astonishing records of intellectual and industrial activity of which history has any record.

Faraday's next contribution to aromatic chemistry consisted in a study of the action of sulphuric acid on naphthalene, or 'naphthaline' as it was then termed—a name which we owe to Dr. John Kidd, who lectured on chemistry at Oxford in the early part of the century, and who accurately described the main properties of the hydrocarbon, which appears to have been first observed in 1819 by Alexander Garden, of Old Compton Street, Soho, where the London Chemical Society had its habitation. The products obtained by Faraday are now known as  $\alpha$ - and  $\beta$ -naphthalenesulphonic acids, the salts of which he described. It is noteworthy that in this year (1826) the Friday evening discourses at the Royal Institution were instituted by Faraday, with a view, as he says, to facilitate our object of attracting the world and making ourselves, with science, "attractive to it," and that this work on naphthalenesulphonic acid was the subject of the first chemical discourse of the series. Unpromising as it might seem, we may be quite sure that Faraday made it attractive.

Although Faraday continued to occupy himself at times with chemical subjects, even to the end of his tenure of the Fullerian professorship at the Royal Institution, he gradually became more and more absorbed in those memorable physical researches with which his name will ever be associated. The more important portion of his chemical work was practically all done before the end of 1826, and, curiously enough, one of the last inquiries with which he concerned himself in that year serves to connect him with Graham, whose services to science began in that year. It happened that Faraday, in 1823, had made some observations, perhaps among the earliest ever made, which served to establish what we now know as the transpiration of gases, but their accuracy had been doubted by Davy, who, three years later, repeated them. Davy's experiments on this subject constitute, in fact, the last ever performed by him in the laboratory of the Royal Institution. Faraday independently repeated the observations of 1823 and established their validity.

Graham's chief work, of course, lay in the borderland between physics and chemistry. The finite extent of the atmosphere; the absorption of vapours by liquids; the law of the diffusion of gases; the motion of gases; the diffusion of liquids; osmotic force; on liquid transpiration; on molecular mobility of gases; the absorption and dialytic separation of gases by colloid septa; on occlusion of gases; hydrogenium—however different may be the titles of his papers, all his work centred round conceptions of atoms and molecules and their motions. Of his contributions to pure chemistry, the most important was that "On the arseniates, phosphates, and modifications of phosphoric acid"—the first of his papers sent to the Royal Society, to which it was communicated by Edward Turner, whom he succeeded a few years later in the Chair of Chemistry at University College. This memoir established the existence of three modifications of phosphoric acid—ortho-, pyro-, and meta-phosphoric acid. The first, or ordinary phosphoric acid, has been known for at least three centuries; pyrophosphoric acid was discovered by Clark, whom Graham succeeded as Lecturer on Chemistry at the Mechanics' Institute, Glasgow; metaphosphoric acid was now made known for the first time. The paper is memorable from the circumstance that it first definitely indicated the idea of *basicity*.

Graham's memoirs on the part played by water as a constituent of salts, and on the constitution of salts, are logically connected with and dependent on this paper. Indeed, nothing is more remarkable in Graham's work than the continuity of idea which pervades it. Just as the long succession of memoirs on the molecular movements of gases and liquids gave a definiteness and precision to

the conception of the intestinal motions in matter, so his work on acids and salts served to establish the constitutional analogy between these substances.

Edward Turner was born in Jamaica in 1798, and after studying medicine at Edinburgh, passed over to Göttingen, where he worked under Stromeyer. In 1824, he became a lecturer in Edinburgh and here published an "Introduction to the Study and Laws of Chemical Combination," which he subsequently worked into his excellent "Elements of Chemistry," one of the standard text-books of the time, and by which he is mainly remembered. In 1828, he was made Professor of Chemistry in the newly-created University of London, now known as University College, and died in 1837 in the fortieth year of his age. Among his pupils was the late Sir Richard Quain, who described him as a lucid lecturer and a good analyst. Turner was indeed an excellent manipulator, and his analytical and determinative work was of a high order. He is especially to be remembered for his determinations of the atomic weights of lead, chlorine, silver, barium, mercury, nitrogen, and sulphur; they were the first atomic weights to be accurately ascertained by a British chemist, and are worthy to be ranked with the determinations of Berzelius. Turner's numbers were not only valuable as constants, but they were of theoretical importance as directly impugning the validity of Prout's hypothesis, which, mainly on the authority of Thomas Thomson, who had sought to support it by what is perhaps the weakest experimental evidence ever put forward, was part of the current doctrine of the time in this country. On Thomson's work, Berzelius had passed what is probably the most scathing criticism he ever uttered: "This work belongs to those few productions from which science will derive no advantage whatever. Much of the experimental part, even of the fundamental experiments, appears to have been made at the writing desk; and the greatest civility which his contemporaries can show its author, is to forget that it was ever published" (*Jahresber.*, 1827, 77).

Turner pointed out (1) that the atomic weights hitherto commonly used by British chemists had been adopted without due inquiry, and that several of the most important ones were erroneous, and (2) that the hypothesis that all equivalents are multiples of a whole number of the equivalent of hydrogen was inconsistent with the state of chemical knowledge at the time, being at variance with experiment. "Under such circumstances, Dr. Prout's hypothesis, as advocated by Dr. Thomson—that all atomic weights are simple multiples of that of hydrogen—can no longer be maintained. I grant most willingly that a system of whole numbers, considered as moderate approximations, may, with advantage, be retained for the use of medical men, students, and manufacturers; but as the strict representative of scientific truth,

applicable to all the purposes of science, this hypothesis is at present untenable. Let me not, however, be misunderstood : I mean simply to affirm that the experiments by which it has been attempted to prove the truth of this hypothesis are inaccurate ; I may go further, and declare it to be not only unsupported by evidence, but to be at variance with the most exact analytic researches which have been conducted. I deny not that some simple relation subsists among atomic weights, and that their ratios may possibly be expressed by some series of numbers ; but at present no one has assigned any physical cause for the existence of such a relation ; no such relation has hitherto been discovered ; nor, as appears to me, has analytical chemistry attained that degree of perfection which can justify anyone in finally asserting or denying its existence." The position thus taken up by Turner is precisely that to which Stas arrived half a century later, after an inquiry which will ever remain a model of analytical skill.

William Hyde Wollaston died on December 22nd, 1828, at the age of sixty-two ; Thomas Young, on May 10th, 1829, aged fifty-six ; and Humphry Davy, on May 29th, 1829, aged fifty-one. The passing away of three such men in the ripeness of their intellectual vigour and in such quick succession, profoundly affected the whole scientific world. They had been colleagues during life, each holding high office in the Councils of the Royal Society, and were, with Dalton, the brightest ornaments of one of the most glorious epochs in the history of physical science in this country. At present, we are only concerned with Wollaston and Davy. On Davy's triumphs, on his mental powers, and on the characteristics of his genius it is unnecessary now to dwell ; with the exception of that of Dalton, there is probably no personality in the history of British chemistry with which we are more familiar. Wollaston is less well known ; his achievements, indeed, were less calculated to strike the popular imagination than those of his great contemporaries. But this silent, austere man, who lived in and for his laboratory and his library, his only relaxation being an occasional evening among his fellows at the Royal Society Club, or at the gatherings of the Royal Society, had a wonderfully clear intelligence and an astonishingly penetrative insight. No man ever more justly earned the title of philosopher. He was not so prolific or so diffuse as Priestley, but his learning was infinitely deeper and broader, and there is not a single branch of the science of his day which he did not illumine and adorn—chemistry, astronomy, optics, mechanics, acoustics, mineralogy, crystallography, botany, physiology, pathology—each in turn was the subject of his intellectual activity. It is, however, only with his chemical work that we have here to do. Reference has already been made to the part which Wollaston's paper, "On

super-acid and sub-acid Salts," played in securing attention to the atomic theory; his "Synoptical scale of chemical equivalents" was of special service to the student and the manufacturer in facilitating the application of the laws of chemical combination to operative chemistry. His "Description of a reflective Goniometer" is a classic in the literature of chemical crystallography and marks an epoch in the history of that subject. His discovery of a process by which platina may be rendered malleable proved of incalculable service to practical chemistry and the arts. Some idea of what that service has been may be gained by recalling what we have secured, and secured only by our crucibles and other vessels of platinum, and by the use of platinum foil and wire, and by imagining what our position would be if we were wholly deprived of these articles. Platinum had been known for some sixty years before Wollaston's time, but as has been stated, "the very properties which made its value certain if it were wrought into vessels, forbade its being easily fashioned into them," and whole cargoes of the native metal are said to have lain unpurchased for years in London as it could not be turned to account. Wollaston, foiled in his attempts to make a living by medical practice, became, as is well known, rich by his process of working platinum which he carried on in secret and with the aid of a faithful old servant in his laboratory, a small detached building at the bottom of his garden in Hunter Street, Brunswick Square.

In the early part of the century, the price of manufactured platinum was less than half its present value. In 1805, platinum crucibles were to be obtained from Mr. Carey, 182, Strand; at 17s. 6d. the ounce, whilst wire was 16s. At the time of the foundation of the Chemical Society, the price of manufactured platinum had more than doubled.

Wollaston first made known his process in the Bakerian lecture of 1828—the year of his death—and the Council of the Royal Society "deemed themselves bound to express their strong approbation of this interesting memoir by awarding a Royal medal to its author, and they anticipate with confidence a general approbation of what they have done." The further development of the metallurgy of platinum in this country is associated with the firm of Johnson, Matthey and Co., who worked platinum for many years before any other commercial manufactory was established. The process of Wollaston appears to have been first worked, sometime between 1800 and 1808, by Mr. Thomas Cock, a relative of Mr. Percival Johnson, who began the refining and manufacture of platinum in Hatton Garden.

Wollaston's name is further connected with the platinum group of metals by his discovery of rhodium, which he published in 1804, immediately after the existence of iridium and osmium had been

announced by Smithson Tennant, and also by his discovery of palladium. The manner in which the last-named metal was made known constitutes one of the most singular episodes in the history of scientific discovery, and affords a curious commentary on certain phases of Wollaston's character. In fact, one or two points in Wollaston's connection with the discovery and working of the platinum metals are somewhat obscure.

In 1803 appeared an anonymous circular which was sent to a number of persons, amongst them the editors of Nicholson's and Tilloch's Journals, stating that a new metal—palladium or new silver—could be purchased from Mrs. Forster, 26, Gerrard Street, Soho, in samples of five shillings, half a guinea, and one guinea each, the price being at the rate of one shilling per grain. Certain of the properties of palladium were given in the advertisement to show that it was "a new noble metal." This announcement attracted the attention of Chenevix, an Irish gentleman, well known as a Fellow of the Royal Society and for his analyses of certain minerals and for his work on oxygenised and hyperoxygenised muriatic acid. The mode adopted to make known a discovery of so much importance, without the name of any creditable person except the vendor, appeared to Mr. Chenevix unusual in science and not calculated to inspire confidence. Accordingly, with a view to detect what he conceived to be an imposition, Mr. Chenevix procured a specimen and eventually the whole quantity which had been left for sale with Mrs. Forster, who, she stated, was totally unacquainted with the person who brought the metallic substance and the printed paper to her house. Chenevix found all the statements in the paper to be correct with the exception of that of the specific gravity, which he stated to be different by one or two per cent. He made a long and elaborate investigation of the matter and concluded that the pretended new metal was a combination of platinum and mercury. He sent in his memoir to the Royal Society, and two evenings were spent in the reading of it.

The Journal Book of the Society, the entries of which were made under the direction of the Secretaries, if not actually by them, gives a *précis* of this paper. We read: "Thus, after having been baffled in his attempts to discover, by analysis, the component parts of this substance, which he (the author) could never bring himself to consider as a new metal, a synthetic process at length led him to the discovery that the whole pretence was an imposition, and that the substance is, in fact, a combination of platina and mercury; in which the latter, while it masks the most characteristic properties in the former, loses the greater number of its own distinctive qualities.

"The singular fact that an alloy of two metals should be produced,

the specific gravity of which is little more than one-half of what it ought to be by calculation, is, no doubt, worthy of particular attention; and as quicksilver was in this process brought to a fixed state under circumstances never before observed, a notion might be entertained that the great desideratum in alchemy, the fixation of mercury, was by no means a visionary object. . . . Those who cultivate chemistry with any degree of ardour, will be gratified to see in this paper the pains taken by the author, and the various modes he has devised, to produce this compound metal in its most perfect state of combination."

A few months later, the editors of the various scientific periodicals received "under cover of the twopenny post," an unsigned paper offering a reward of £20 for the artificial production of palladium. The editor of *Nicholson's Journal* says the paper, "is written in the same hand as a note which covered a small piece of palladium mentioned to have been received by me last midsummer. Upon inquiry, I find that Mrs. Forster has received the sum of £20 with instructions conformable to this paper." The paper ran as follows:—

December 16, 1803.

"SIR,

"As I see it said in one of your journals, that the new metal I have called palladium, is not a new noble metal, as I have said it is, but an imposition and a compound of platina and quicksilver, I hope you will do me justice in your next, and tell your readers I promise a reward of 20£ now in Mrs. Forster's hands, to any one that will make only 20 grains of real palladium, before any three gentlemen chymist's you please to name, yourself one if you like.

"That he may have plenty of his ingredients, let him use 20 times as much quicksilver, 20 times as much platina, and in short of anything else he pleases to use: neither he nor I can make a single grain.

"Pray be careful in trying what it is he makes, for the mistake must happen by not trying it rightly.

"My reason for not saying where it was found, was, that I might make some advantage of it, as I have right to do.

"If you think fit to publish this, I beg you to give the names of the umpires, as I have desired Mrs. Forster to keep the money till next midsummer, and to deliver it only in case they can assure her that the real metal is made by a certificate signed by you, and by them, on this check.

"I hope a little bit of whatever is made may be left with Mrs. Forster."



Mr. Nicholson nominated Hatchett and Edward Howard to join himself as judges of the product which might be made in their presence; but the £20 was never claimed, and in 1805, Wollaston, in a memoir contributed to the *Philosophical Transactions*, announced that he was the discoverer of the new metal, to which he had given the name palladium, "from the planet which had been discovered, nearly at the same time, by Dr. Olbers."

What was Wollaston's motive in bringing his discovery to the notice of the scientific world in so extraordinary a manner can only be surmised. From the account of his memoir given in the Journal Book of the Society, in which no mention is made of Chenevix and his work, he refers to the "concise delineation of its character" given in the advertisement of the metal, in which he says he "avoided directing the attention of chemists to the source from where it had been obtained, and thereby reserved to himself a more deliberate examination of many phenomena that yet remained unexplained in the analysis of platina, by which he was subsequently led to the discovery of rhodium." No proper explanation was given of the circumstance that he, as Secretary of the Society, allowed Chenevix's paper to appear in the *Transactions*. It must have been his duty actually to read this paper at the two meetings when it was brought before the Fellows; he must also have been responsible for the account which appears in the Journal Book, and which, as one now peruses it, in the light of what subsequently happened, is almost cutting in its sardonic humour and irony. It has been stated that Wollaston did all in his power to persuade Chenevix to withhold or withdraw his paper. Be this as it may, there is no doubt that Chenevix keenly felt the humiliation he suffered. He retired to the Continent, and all his subsequent papers were published in France.

In the year of Davy's death, Edward Turner wrote, "The æra of brilliant discovery in chemistry appears to have terminated for the present." Although the number of workers in the science was probably greater than during the first few years of the century, the volume of chemical literature actually produced, judged by the number of contributions to the various societies and to scientific periodicals, had been steadily declining during the previous ten years, and was actually not much more than half what it was in 1802. The work of the first quarter of the century had, in fact, been that of the pioneers, and it was now necessary to secure and consolidate what had been gained rather than to push on into new territory. "The time is arrived," continues Turner, "for reviewing our stock of information, and submitting the principal facts and fundamental doctrines of the science to the severest scrutiny. The activity of chemists should now, I conceive,

be especially employed, not so much in searching for new compounds or new elements, as in examining those already discovered; in ascertaining with the greatest possible care the exact ratio in which the elements of compounds are united; in correcting the erroneous statements to which inaccurate observation has given rise; and exposing the fallacy of opinions which partial experience or false facts have produced." Stoichiometrical considerations were, in fact, becoming of increasing importance. The atomic theory was now a part of the settled doctrine of chemistry. To use the words of Davy, chemistry had now passed under the dominion of the mathematical sciences. The exact numerical relations of the elements and their combinations, both by weight and by volume, Prout's hypothesis and all that it implied, were types of the questions which seemed most urgently to require solution. The idea of stating the course of chemical change with a more mathematical precision than had hitherto been possible is reflected, too, in the attempts which were made at about this period to express such changes by means of equations. Chemical symbols have been used from time immemorial, but the notion of attaching a definite numerical value to them had a rational basis only after the promulgation of the atomic theory.

Berzelius is usually credited with having been the first to suggest, in principle, the system of notation at present employed by chemists, although there is a tradition in Glasgow that the merit should be ascribed to Dr. Thomas Thomson. Herschel, in his paper on "Hyposulphurous acid" in the *Edinburgh Philosophical Journal* for 1819, uses algebraic expressions to describe the reaction between silver nitrate and calcium thiosulphate. The idea of using a mathematical notation to express the chemical composition of substances and their mutual actions, although in common use in Sweden, France, and Germany, for a time made little progress in England, partly from the conservatism of chemists, who, like Richard Phillips, failed to perceive its necessity or convenience, and to whom the language of symbols

" . . . was a Babylonish dialect  
Which learned *chemists* much affect;  
It is a party-coloured dress  
Of patch'd and piebald languages;  
'Tis English cut on Greek and Latin,  
Like fustian heretofore on satin;"

and partly from the strictures of mathematicians, chief among whom was Whewell, who condemned the Berzelian system for what he regarded as its "gross anomalies" and "disfigurements," and its want of "mathematical symmetry and consistency"—"a system which violates mathematical propriety so entirely that it must always be disagreeable

to see an example of it, for any person who has acquired the first rudiments of algebra."

Whewell, whose "forte was science, and whose foible was omniscience," of course recognised that a mathematical notation might be of the greatest service in chemistry, and, indeed, could not ultimately be dispensed with, and he made a vigorous attempt "to purify and improve the foreign system." One of the chief rocks of offence to Whewell was the method adopted by Berzelius of connecting the symbols of the elements to represent compound substances. Chemical combination is essentially an operation of addition, whereas the symbolic notation, if understood algebraically, would indicate that the constituents were multiplied by each other. There is not much force in this objection, although, as Whewell points-out, we probably owe to the symbols being read algebraically the ambiguity of the words *factor* and *product*, which are sometimes used to express the ingredients producing a chemical compound by their addition, as well as the compound itself, but which in algebra properly refer to parts producing a number by multiplication. Still more objectionable to Whewell was the use of the sign + ; this he characterised as "a wanton and superfluous violation of analogy."

Whewell's objections were rather more pedantic than practical. It was pointed out that the juxtaposition of symbols and the employment of an index figure, as practised by Berzelius, would lead the chemist into no error, because their subjects are not susceptible of algebraic powers, or of being multiplied into each other.

On general grounds, too, Whewell's system failed to commend itself to chemists, even to those who were not unmindful of the mathematical proprieties. It only approximated to mathematical consistency, and failed altogether as regards brevity and clearness. The multiplication of lines and brackets which it entailed, although algebraically just, gave a perplexing appearance to the formula, and destroyed its graphic character. The unvarying sign + alternately with every letter was also objectionable. Whewell, who was not insensible to these defects in his system, suggested a method of contraction, but the compromise failed to realise the graphic perspicuity of the Berzelian notation, whilst, as an analytical expression, it was inferior to the extended system from which it was evolved. Whewell, moreover, avowedly put it forward as more suitable for the purposes of mineralogy than of chemistry, and the objection was naturally raised that a system which required new contrivances and contractions to suit different points of reasoning, and was so partial and so incomplete an expression of chemical composition in general, was certain to lead to interminable confusion and difficulty.

The serial chemical literature of the early thirties contains a number of interesting papers on chemical notation, not only by Whewell, but by Phillips, Prideaux, Warington, and Graham, and the merits of the various systems proposed were fairly discussed, with the result that the Berzelian method was at length universally adopted. As an example of the confusion which reigned at the time, we give, from one of Phillips's papers, the composition of common phosphate of soda as expressed in the different systems of notation then in vogue.

Berzelius .....	$\ddot{\text{N}}\text{a}\ddot{\text{P}} + 24 \text{ Aq.}$
„ .....	$\text{N}\text{a}^2\ddot{\text{P}} + 24\dot{\text{H}}.$
Graham .....	$\text{N}\text{a}^2\dot{\text{H}}^2\ddot{\text{P}}.$
Rose.....	$\text{NaO} + \text{PO}^5 + 24\text{HO}.$
Whewell .....	$\text{N} + p' + 24 \text{ q.}$
Brande.....	$\text{S} + p' + 24 \text{ q.}$
Turner .....	$\dot{\text{S}}\text{o} + \text{P} + 2\frac{1}{2}\text{O} + 24 \text{ aq.}$
Johnstone .....	$\text{P} + \dot{\text{S}}\text{o} + 24\dot{\text{H}}.$
Prideaux .....	$\text{N}\ddot{\text{P}} + 24 \text{ Aq.}$
Warington .....	$\overset{\circ}{\text{P}}\text{o} + \overset{\circ}{\text{S}}\text{o} + 24\text{H}^\circ.$

With the exception of Graham, it cannot be said that British or Irish chemists made any very remarkable contributions to science during the decade from 1830 to 1840. The number of workers was doubtless greater than at any previous period of the century. The volume of literature, as measured by the number of papers published, was more than double that of the first decade—one of the most momentous periods of our chemical history. But the efforts of workers at the time were spent more on points of detail, on the filling in of little gaps in the chemical structure, as it then existed, than in attempts at new developments.

Thomas Clark, mainly remembered for his method of determining the hardness of water, and for his discovery of pyrophosphoric acid, was studying the metallurgy of iron. Apjohn, whose name is best known in connection with his formula for determining the dew-point from the indications of the wet bulb hygrometer, contributed a few papers on mineral chemistry; Daubeny, a professor of chemistry to botanists, and a professor of botany to chemists, occupied himself principally with geological and botanical chemistry; Colonel Yorke studied the action of water on lead; Everitt investigated the behaviour of dilute sul-

phuric acid with potassium ferrocyanide, and discovered the salt which is associated with his name; Johnston made analyses of mineral substances of organic origin, investigated paracyanogen, certain cyanides, and double haloid salts; Kane analysed a few minerals and inorganic salts, the chlorides of iodine, and studied the action of ammonia on the chlorides and oxides of mercury, the composition of essential oils, and the nature of wood spirit. Penny made a remarkably accurate series of atomic weight determinations of chlorine, nitrogen, potassium, and sodium, which served still further to strengthen the case against the hypothesis that all equivalent numbers are simple multiples of that of hydrogen; and Gregory, the successor of Graham at the Andersonian College, a follower of Liebig, and one of the earliest chemists to introduce his methods into Britain, occupied himself with the study of pharmacological and organic products, the analysis of petroleum, and the destructive distillation of caoutchouc. Other chemical workers at this period were Pepys, Porrett, Edmund Davy, Brooke, Cooper, Daniel, John Mercer, William Herapath, Walter Crum, William West, Hennell, Scanlan, Teschemacher, Hugh L. Pattinson, Warrington, Andrews, Richardson, Robert D. Thomson, Denham Smith, Golding Bird, Solly, Fownes, Stenhouse, George Wilson, and Griffin.

But the general condition of scientific chemistry with us during this period was, no doubt, accurately characterised by Liebig, when he wrote to Berzelius in 1837: "*Ich bin einige Monate in England gewesen, habe ungeheuer viel gesehen und wenig gelernt. England ist nicht das Land der Wissenschaft, es existirt dorten nur ein weitgetriebener Dilettantismus, die Chemiker schämen sich Chemiker zu heissen, weil die Apotheker, welche verachtet sind, diesen Namen an sich gezogen haben . . . Graham macht auch in wissenschaftlicher Hinsicht die schätzbarste Ausnahme, er ist ein vortrefflicher Mensch, auch Gregory, der an seine Stelle in Glasgow gekommen ist.*"

It was at this low ebb in our fortunes that the Chemical Society was founded. It might seem, at first sight, an unpropitious time at which to launch a new Society for the purpose of publishing the work of chemical investigators, when chemical investigation itself was so languidly pursued. But the seventy-seven gentlemen from all parts of the kingdom who enrolled themselves as the founders of the Chemical Society appeared to have had a robust faith in its ultimate success, and in the influence it was bound to exercise in stimulating chemical inquiry in these islands.

How far their faith was well founded—how far indeed this Society has succeeded in stimulating chemical research in this kingdom, I may possibly have an opportunity of showing on some future occasion. I

hope also to be able to offer some account of the development of our means of teaching chemistry in this country during the century.

SIR HENRY ROSCOE, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the *Transactions*.

Prof. LIVEING, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Prof. TILDEN, F.R.S., the Treasurer, in giving an account of the Balance Sheet which he laid before the Society, duly audited, said :—

The receipts had been :—By admission fees and subscriptions, £4088; by sale of Journal and advertisements, £781 15s. 6d.; and by dividends on invested capital, £444 13s. 7d. The expenses had been :—On account of the Journal, £3388 12s. 11d.; on account of the Proceedings, £171 14s. 7d.; on account of the preparation of a new Card Catalogue, £35 9s. 2d.; on account of the Library, £286 17s. 3d.; House expenses, including the re-decoration of the Building, £543 5s. 11d.; the total expenditure being £4993 13s. 1d. Grants amounting to £192 had been made to Fellows from the Research Fund during the year.

Attention was directed to the fact that the net income of the Society for the year being £5,371 1s. 5d., and the expenses £4,993 13s. 1d., the surplus is only £377 8s. 4d. This is considerably less than the amount, £578, of the Composition and Admission Fees which ought to be regarded as capital. In view of the steadily increasing cost of the Society's publications, the recurrence of the heavy charge for the Decennial Index, and the growth of the Library, economy will have to be practised to keep the finances of the Society in a healthy condition. The Treasurer appealed to authors of papers to assist in keeping down the cost of composing and correcting the proofs of papers communicated to the Society. At the present time the average cost of corrections amounts to more than one-third the charges for putting manuscript into type. A little more care exercised by authors in preparing for the press would result in a substantial reduction in the cost of printing.

Prof. ODLING, F.R.S., proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Dr. RUSSELL, F.R.S., and carried.

The TREASURER, in responding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. PAGE.

Prof. H. B. DIXON, F.R.S., proposed a vote of thanks to the Officers and Council.

Prof. WABINGTON, F.R.S., seconded the motion, which was unanimously adopted.

Prof. DUNSTAN, F.R.S., responded on behalf of the Council.

Prof. DEWAR, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Mr. GROVES, F.R.S., and carried.

Dr. WYNNE, F.R.S., responded.

Dr. DYER and Mr. FRISWELL were appointed Scrutators, and a ballot was taken for the election of Officers and Council for the ensuing year. The Scrutators having presented their report to the President, he declared that the following had been duly elected :—

*President* : T. E. Thorpe, Ph.D., D.Sc., LL.D., For.Sec.R.S.

*Vice-Presidents who have filled the office of President* : Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S. ; H. E. Armstrong, Ph.D., LL.D., F.R.S. ; A. Crum Brown, D.Sc., LL.D., F.R.S. ; Sir W. Crookes, F.R.S. ; James Dewar, M.A., LL.D., F.R.S. ; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S. ; J. H. Gladstone, Ph.D., D.Sc., F.R.S. ; A. Vernon Harcourt, M.A., D.C.L., F.R.S. ; H. Müller, Ph.D., LL.D., F.R.S. ; W. Odling, M.A., M.B., F.R.S. ; W. H. Perkin, LL.D., Ph.D., F.R.S. ; Sir H. E. Roscoe, D.C.L., LL.D., F.R.S. ; W. J. Russell, Ph.D., F.R.S. ; A. W. Williamson, LL.D., F.R.S.

*Vice-Presidents* : E. Divers, M.D., D.Sc., F.R.S. ; C. E. Groves, F.R.S. ; G. D. Liveing, M.A., D.Sc., F.R.S. ; T. Purdie, Ph.D., F.R.S. ; T. Stevenson, M.D. ; John M. Thomson, LL.D., F.R.S.

*Secretaries* : Wyndham R. Dunstan, M.A., F.R.S. ; A. Scott, M.A., D.Sc., F.R.S.

*Foreign Secretary* : Raphael Meldola, F.R.S.

*Treasurer* : William A. Tilden, D.Sc., F.R.S.

*Other Members of Council* : H. Brereton Baker, M.A. ; F. D. Chattaway, Ph.D., D.Sc. ; Frank Clowes, D.Sc. ; J. Norman Collie, Ph.D., F.R.S. ; A. E. Dixon, M.D. ; H. J. H. Fenton, M.A., F.R.S. ; W. Gowland ; C. T. Heycock, M.A., F.R.S. ; D. Howard ; Rudolph Messel, Ph.D. ; W. J. Pope ; James Walker, D.Sc.

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## THE TREASURER IN ACCOUNT WITH THE CHEMICAL

DR.

	£	s.	d.	£	s.	d.
Balance at Bank, March 25th, 1899 .....	449	8	4			
„ in hands of Treasurer .....	0	1	8			
Transferred from Deposit Account .....				449	9	7
Receipts by Life Compositions, Admission Fees and Subscriptions from March 25th, 1899, to March 24th, 1900:—				500	0	0
Life Compositions—2 at £30; 2 at £20; 1 at £10.....	110	0	0			
117 Admission Fees .....	468	0	0			
1 Subscription for 1896 at £2 .....	2	0	0			
2 „ „ 1897 „ £2 .....	4	0	0			
91 „ „ 1898 „ £2 .....	182	0	0			
1 „ „ 1899 „ £2 .....	1	0	0			
618 „ „ 1899 „ £1 .....	1,226	0	0			
3 „ „ 1899 „ £2 .....	8	0	0			
1,038 „ „ 1900 „ £1 .....	2,076	0	0			
10 „ „ 1900 „ £2 .....	10	0	0			
3 „ „ 1901 „ £1 .....	6	0	0			
„ „ 1901 „ £2 .....				4,088	0	0
Sale of Journals .....	660	16	8			
„ Proceedings .....	18	13	0			
„ General Index: To the Public.....	30	3	0			
„ „ To Fellows.....	12	4	0			
„ Old Stock .....	3	0	0			
Proceeds of Advertisements in Journal .....	52	19	3			
Subscription from the Society of Chemical Industry to June, 1899 .....	9	9	0	781	15	6
„ „ „ Public Analysts to January 1st, 1900 .....	13	2	6			
„ „ „ Physical Society to January 1st, 1900 .....	19	19	0			
Repayment of Income Tax.....				42	10	6
Year's Dividends on £6,780 Metropolitan Board of Works 3½ per cent. Stock .....	227	14	0	14	1	10
„ „ £4,000 Consols.....	79	15	0			
„ „ £1,050 London and North-Western Railway Debenture Stock .....	80	9	0			
„ „ £1,520 14s. 3d. Cardiff Corporation Stock .....	44	2	0			
„ „ £1,400 India 2½ per cent. Stock.....	25	7	6			
„ „ £2,358 Midland 2½ per cent. Preference .....	28	9	10			
Interest on Bank Deposit .....	8	16	3			
Sale of £4,000 Consols. ....				444	18	7
				4,142	10	0

Assets.	Estimated Value.
March 24th, 1900.	
Balance at Bank (Current Account) .....	826 15 3
„ „ (on Deposit) .....	500 0 0
„ „ in hands of Treasurer .....	0 2 8
£6,780 Metropolitan Board of Works 3½ per cent. Stock .....	7,436 13 0
£1,050 London and North-Western Railway Debenture Stock .....	1,118 5 0
£1,520 14s. 3d. Cardiff Corporation 3 per cent. Stock.....	1,513 2 2
£1,400 India 2½ per cent. Preference .....	2,010 3 11
£2,358 Midland 2½ per cent. Debenture Stock .....	2,062 0 0
£4,000 Consols .....	1,253 0 0
	<u>£16,710 2 0</u>

£10,463 1 0



SOCIETY, FROM MARCH 25TH, 1899 TO MARCH 24TH, 1900.

CR.

*Expenses on Account of the Journal and Proceedings.*

	£	s.	d.	£	s.	d.
Salary of Editor .....	250	0	0			
Sub-Editor .....	200	0	0			
Sub-Editor's Assistant .....	10	10	0			
Editorial Postages .....	14	8	8			
Abstractors' Fees .....	418	1	1			
Printing of Journal .....	1,772	5	1			
Printing of Advertisements .....	15	4	4			
Printing Wrappers .....	100	8	0			
Distribution of Journal by Printers .....	879	8	2			
Society .....	12	8	10			
Authors' Copies .....	79	5	0			
Indexers' Fees (1899 and 1900 Index) .....	102	10	2			
Illustrations for Journal .....	84	14	0			
				8,388	12	11
Printing of Proceedings .....	118	9	8			
Distribution of Proceedings .....	58	4	11			
				171	14	7
Publishers' Commission .....	71	7	2			
Advertising Agents' Commission .....	7	19	0			
				79	6	2

*Expenses on Account of the Library Catalogue.*

Salaries .....	88	0	8			
Petty expenses .....	2	2	6			
				85	9	2

*Expenses on Account of the Library.*

Salary of Library Assistant .....	52	0	0			
Books and Periodicals .....	146	2	11			
Binding .....	88	14	4			
				286	17	8
Salary of Assistant Secretary .....	194	8	4			
Pension to Mr. Hall .....	190	0	0			
Miscellaneous Printing .....	52	14	5			
Stationery .....	18	7	11			
Stocktaking .....	5	8	0			
Legal Charges .....	10	0	6			
Grants to Victor Meyer Memorial Fund .....	10	10	0			
Repayment of Subscription for 1898 .....	2	0	0			
Expenses on Account of Dinner to Past Presidents on November 11th, 1898:						
Report of Speeches .....	7	1	0			
Davy Bust, Remodelling and Casting (Balance of Account) .....	4	16	0			

*House Expenses.*

Providing Refreshments .....	20	15	2			
Lighting the Building.....(Gas, £28 5s. 10d.; Electric Light, £24 1s. 7d.) .....	52	7	5			
Heating the Building (Coals) .....	20	0	2			
Cleaning .....	15	0	0			
Repairs and Decoration .....	841	4	2			
Petty House Expenses .....	20	8	9			
House Porter's Wages .....	65	0	0			
Uniform .....	6	7	0			
Annual Fee to Gate Porter .....	2	2	0			
Inhabited House Duty .....	0	6	8			
				548	5	11
Bank Charges on Country and Foreign Drafts .....	1	2	4			
Treasurer's Stamps and Drafts .....	11	10	10			
Treasurer's Petty Cash Disbursements .....	0	8	7			
Assistant .....	10	0	0			
Postage Account: Office and Secretarial Postages, £9 9s. 5d.; Postal Cards and Stamped Envelopes (Clay), £20 18s. 9d. ....	30	8	2			
Transferred to Deposit Account .....	500	0	0			
Purchase of £2,358 Midland Railway 2½ per cent. Preference Stock .....	2,072	8	0			
£2,400 Bristol Corporation 2½ per cent. Debenture Stock .....	2,070	2	0			
Balance at Bank .....	826	15	8			
in hands of Treasurer .....	0	2	8			

£10,463 1 0

Audited with vouchers and found correct.  
24th March, 1900.

ARTHUR W. CROSSLEY.  
FREDERIC JAS. M. PAGE.  
E. W. VOELCKER.



## OBITUARY NOTICES.

PETER WAAGE, the son of Captain Peter Waage, of the Norwegian Merchant Service, was born at Flekkefjord, a picturesque little village in South Norway, on the 29th of June, 1833. He received his education in the Bergen Grammar School, and entered the University of Christiania in 1854. Like many others, he entered chemistry through the portals of medicine, but even as a medical student, chemistry and mineralogy had more attraction for him, and although he passed the first of his medical examinations, he abandoned the study of medicine for that of natural science. In his fourth year at the University, he won the gold medal awarded each year for a special essay. On that occasion, the essay was prescribed on "The theory of the radicles of oxygenated acids," and Waage's essay was held worthy of the prize. It was afterwards published in the *Nyt Magazin for Naturvidenskab*. It gained for him the position of "University Stipendiat," analogous to that of "Privatdocent" of the German Universities, but differing by the receipt of salary. As such he visited Germany, and was one of the numerous roll of Bunsen's students. On his return, in 1862, he succeeded, as Professor at Christiania, Adolf Strecker, who in that year was called to the vacant chair at Tübingen. Shortly after his appointment, in 1864, he published, in conjunction with his brother-in-law, Guldberg, Professor of Mathematics in the same University, a first draft of the memoir which made him famous ("Videnskabs Selskabs Forhandlingen"). A year later, the memoir formed his University oration, and it was published in French in 1867 under the title, "Études sur les Affinités Chimiques." Twelve years later, a revised edition of the memoir appeared in the *Journal für praktische Chemie*, for by that time attention had been drawn to the value of the work, and the French edition was exhausted. The fundamental principle underlying this work is a very simple one; it is known as the "Law of Mass-action." Guldberg and Waage developed the thesis that chemical action is proportional to the amounts of acting substances present; by the expression "amount," is understood quantity in unit volume. The intensity of the action is conditional on the amount of each substance, and if two active substances be present, it is proportional to their product. It is also affected by temperature, the nature of the reacting substances, and other circumstances; these, however, may be represented by a factor. If this factor be termed  $K$ , and the masses per unit volume of the acting substances  $p$  and  $q$ , then the chemical affinity or "force" is represented by  $Kpq$ . Equilibrium sets in when the "force" tending to cause the reaction to take place is balanced

by an equal and opposite "force," when  $Kpq = K'p'q'$ . This doctrine was developed and illustrated by numerous experimental verifications.

Waage was also interested in the application of chemistry to the welfare of his country. He devised a method of determining the percentage of alcohol in beer by an instrument termed the "ebulliometer," and endeavoured to have it applied by the Government to the valuation of the alcoholic strength of beer with a view to its progressive taxation. The author remembers how, in 1881, he concocted a letter in English, at Waage's request, to Mr. Gladstone, in the hope of inducing him to extend the progressive tax on light wines to beer. Waage was an ardent advocate of temperance principles. Another effort made to apply chemistry for the benefit of his people was the devising a process for making "fish-meal" a nutritive article of food. But public taste refused it, and its manufacture is now abandoned. He was also largely interested in social and religious endeavours to educate and refine the people, and was president of the society analogous to our "Young Men's Christian Association."

Somewhat rough in external appearance, Waage's kindliness of manner, and heartiness and earnestness in all he said and did, impressed one with a sense of his power of influencing men. He will be known by his one great work, and so long as the history of chemistry is read, the opening chapter on the laws of chemical affinity will be associated with the names of Guldberg and Waage. W. R.

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WILLIAM HARKNESS, formerly a Superintending Analyst of the Inland Revenue branch of the Government Laboratories, was born in Edinburgh on March 30th, 1834, and entered the Government Laboratory in 1860, becoming an Analyst on the permanent staff in 1867, and a Superintending Analyst in 1884, a post which he held until his retirement in 1897. He was specially known in the laboratories for his abilities as a microscopist, particularly in the detection of vegetable substance as adulterants of tobacco, tea, coffee, &c. He devoted much attention to the subject of concentrated foods, and was frequently consulted in the fitting out of various polar expeditions. He was a Fellow of the Royal Microscopical Society, of the Society of Chemical Industry, and of the Institute of Chemistry, and served on the Council of the latter body. He was elected a Fellow of the Chemical Society on December 16th, 1875, and died in Arran on September 5th, 1899. His kindly disposition and unvarying courtesy endeared him to a large circle of friends.

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DR. J. F. HODGES, of Belfast, who was elected into the Society in 1844, died on the 13th December, 1899. The son of a solicitor belonging to a very old County Down family, he was born in 1815 at Downpatrick. On leaving school, he was apprenticed to a medical practitioner in his native town, and afterwards studied in Dublin at the Royal College of Surgeons and Trinity College, and subsequently in Glasgow, where he made the acquaintance of Graham, who strongly advised him to turn to chemistry. Returning to his native country, he commenced the practice of medicine in Newcastle, thence he removed to Downpatrick, and was instrumental in founding the Mechanics' Institute in that town—one of the first ever established in Ireland. He developed a deep interest in agriculture, which he rightly regarded as one of the leading industries in Ireland. Impressed with the idea that he might turn his scientific aptitude to good service in connection with that industry, he went to Germany and studied under Liebig, with whom he contracted a friendship which terminated only with Liebig's death. After taking his degree at Giessen, he returned to Downpatrick, and commenced lecturing on "What Science can do for the Irish Farmer." His lectures, which were published at the expense of the Marquis of Londonderry—grandfather of the present peer—attracted much attention, and the interest they aroused throughout the North of Ireland led to the formation, in 1845, of the Chemico-Agricultural Society of Ulster—an organisation based upon the model of the Highland Agricultural Association of Scotland.

Not long afterwards, Dr. Hodges became the editor of the *Irish Agriculturist*, a weekly journal published in Belfast.

In 1845, he was appointed Professor of Chemistry in the old Belfast College as successor to Andrews, who became Vice-President of Queen's College. On the Government endowing a Chair of Agricultural Chemistry in the latter college, Dr. Hodges was appointed its first occupant, as well as Lecturer on Medical Jurisprudence, and both of these positions he held up to the time of his death. By his demise, the last of the original professors of Queen's College has passed away.

Amongst his writings may be mentioned "First Steps in Chemistry," the "Structure and Physiology of Animals of the Farm," and "Lessons in Chemistry for Farmers and Teachers." He contributed numerous reports to the British Association, and at the Belfast meeting read a paper on "The Organic Constituents of the Flax Plant." He was a frequent contributor to our Journal. Amongst his papers may be mentioned the "Pharmaceutical and Chemical Characters of the Peruvian Matico," "Composition of Tea and Tea-soils from Cachar," and the "Composition of the Fibre of the Jute Plant, and its use as a Textile Material."

He was one of the founders of the Royal College of Chemistry in  
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London, and, at the request of the Council of that Institution, proceeded to Germany to offer the Chair of Chemistry to Will, who, as is well known, declined it in favour of Hofmann.

Dr. Hodges held a number of public appointments, and, in spite of his great age, was active in the discharge of his duties up to within a few days of his death.

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GEORGE HENRY OGSTON was born in 1827, and was educated at Putney Engineering College. He afterwards became assistant to Professor Graham at University College. In 1846, he commenced his work with Professor J. T. Way on the composition of plant-ash. The investigation was begun at the Royal Agricultural College, Cirencester, but the greater part of the work was afterwards carried out in London. This investigation belongs to the classics of agricultural chemistry. It was conceived in a thoroughly scientific spirit, and was comprehensive in its scope. The results were given in four reports to the Royal Agricultural Society by Way and Ogston, and were published in the Journal of the Society in 1846, 1847, 1848, and 1850. The greater part of Mr. Ogston's life was devoted to technical and commercial chemistry. He was one of the earliest fellows of the Institute of Chemistry, and served on the Council. He died on July 15th, 1899. R. W.

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Dr. WILLIAM MARCET, F.R.S., who was elected a Fellow of this Society on February 7th, 1853, and who died at Luxor on March 4th of this year at the age of 72, is chiefly known for his work on the chemical aspects of physiology and pathology, especially in regard to the chemical nature of human excreta in health and disease, and on the chemistry of digestion. Some of his contributions on these subjects appeared in our Journal. In 1869, he published a remarkable paper on the temperature of the human body at different altitudes, both in a state of repose and during the act of ascending. He will, however, mainly be remembered by his work upon the function of respiration at various altitudes, which he afterwards elaborated into an extended memoir on human respiration in general, and made the subject matter of the Croonian Lectures delivered by him before the Royal College of Physicians in 1895. Dr. Marcet directed much attention to the physiological and pathological properties of alcohol. He also concerned himself with the subject of dietetics, and published a work as far back as 1856, "On the composition of food, and how it is assimilated, with practical directions for its analysis"; in 1867 he described a method for peptonising meat, and showed how the product ~~might~~ be employed in diseases of the stomach. He also paid

considerable attention to climatology, with special reference to the hygienic conditions of the principal Southern and Swiss health resorts.

Dr. Marcet was a highly cultured man, of wide sympathies, and of a genial, hospitable disposition. His loss will be especially felt by the members of the Physiological Society, at whose meetings he was a constant attendant.

Dr. ROBERT OXLAND was elected a member of the Chemical Society in 1851. He died on April 11th, 1899. He was one of the earlier public analysts, having been appointed in 1878 at Plymouth and Devonport. His special work lay chiefly in the domain of metallurgy, in which he devised a wet method for the extraction of copper from ores, also a mill for the concentration of cassiterite when associated with metallic sulphides and arsenides. He is chiefly known, however, as the joint inventor with Mr. John Hocking of the "revolving calcining furnace" which bears their names.

W. G.

RICHARD TAYLER PLIMPTON was born on July 10th, 1856, at Clapham. He was the only son of William Plimpton and Eliza Anna *née* Tayler, and had one sister.

After attending a preparatory school, he was for four years a pupil at University College School, where he acquired a taste for chemistry in the class-room of Mr. Temple Orme.

He matriculated in 1874, and then proceeded to University College, but, unlike the majority of his fellow students, he thought it better to specialise at once, rather than spend time over the large range of subjects then required for a London degree. At University College, he devoted himself almost entirely to the study of chemistry under the direction of Prof. A. W. Williamson and Dr. Charles Graham.

In January, 1878, Plimpton went to Germany, and worked for six months in Kekulé's laboratory at Bonn, and afterwards with Prof. Theodor Zincke at Marburg, where, in 1880, he obtained his doctor's degree with a dissertation on the action of ammonia and the amines upon naphthaquinone.

From Marburg, Plimpton went to Paris, where he worked for a year in the laboratory of Prof. Wurtz, and published some researches on active and inactive amylamines obtained from fusel oil. In 1881, he returned to London, and took a bench in the new chemical laboratory at University College, but he was very soon appointed assistant by Prof. Williamson, and subsequently became Lecturer and, in 1884, Assistant-Professor of Chemistry at the College, a post which he retained after Prof. Ramsay had succeeded Prof. Williamson in the chair

of chemistry. While at University College, he contributed to this Journal a number of papers on the halogen and metallic derivatives of acetylene.

In 1894, Plimpton was appointed Lecturer on Chemistry at the Middlesex Hospital Medical School, and had barely held the Middlesex Lectureship for six years when, on December 21st, 1899, he died suddenly as he was in the act of entering his laboratory.

Plimpton was a member of the Council of the Chemical Society from 1888 to 1891. As a teacher, he strongly dissuaded his pupils from undertaking any kind of independent work until they had acquired a thoroughly practical knowledge of general and analytical chemistry. His lectures on quantitative analysis were particularly appreciated, and he devised many new or modified methods of analysis, such as his well-known method for the estimation of halogens in organic compounds. Plimpton was of an exceedingly amiable disposition, and his cheerful countenance will be missed, not only by his friends in London, but also in the little colony at Hindhead where he used to spend his week-ends.

His death, at the early age of forty-three, has deprived the world of one who would fain have seen all men at peace with one another, and who kept that end constantly in view.

H. F. M.

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LIEUT.-COLONEL HENRY CHARLES REYNOLDS, R.E., was the son of Major-General John William Reynolds, 11th Hussars, Fellow of this Society, of whom an obituary notice appeared in the Journal in 1876, and who, working under Hofmann's guidance, discovered the hydrocarbon propylene. Henry C. Reynolds was born at Belfast in 1842; he was educated at Eton, and at the Royal Military Academy, Woolwich. In 1862, he received his commission in the Royal Engineers. He served for twelve consecutive years in India, chiefly in designing and constructing bridges, and also in making roads up the numerous ghâts of that country. He was a keen sportsman, and always shot his tigers on foot; many fell to his hand. In 1876, he returned home, and, in 1877, was placed in charge of the Ordnance Survey of the Western District, of which the headquarters were at Clifton, near Bristol. Shortly after his return, he married the daughter of Wildman Goodwyn, Esq., late Judge in the Supreme Court of Madras. In 1882, he was ordered to Ireland, where he remained two years on garrison duty, and superintended the building of the new barracks at Belfast. In 1884, he retired with the honorary rank of lieutenant-colonel. He was subsequently offered the post of commander of a regiment of miners, but was reluctantly obliged to decline it.



The pursuit of science for its own sake had always been Reynolds' ambition, and on attaining the requisite leisure, he proceeded to study chemistry at University College, Bristol, where he worked in the laboratory for nearly five years, and made himself a competent chemist. The science of accurate measurement had always an attraction for him, and as soon as he had acquired the requisite knowledge and skill in manipulation, he devoted his attention to the determination of equivalents of elements. In conjunction with the writer, he undertook an investigation on the equivalent of zinc, measuring the volume of hydrogen obtained on treating the metal with dilute acid. The number he obtained for the atomic weight, 65.48, differs but little from that chosen by Richards in his last revision of atomic weights, namely, 65.40. The results of this research were published in the Transactions for 1887. In order to superintend his children's education, Colonel Reynolds removed, in 1889, to Cheltenham, where he fitted up a commodious private laboratory. But long exposure to Indian climate had told upon his health and energy, and, although he began experiments on the ratio of hydrogen and nitrogen in ammonia, he was unable to complete them. He died on May 1st, 1899, of lung disease, complicated by frequent returns of the malarial fever contracted in the Indian jungles—an insidious foe from whose attacks he had never thoroughly recovered.

Colonel Reynolds is an instance, not uncommon in this country, but almost unknown abroad, of a man forming an ideal in his early days, and endeavouring to attain it when opportunity offered. He was a kindly, courteous man, respected and beloved by all who were privileged to know him, and it is to be regretted that his opportunities and training were not compatible with his aspirations. He had it in him, had circumstances been otherwise, to have become a chemist of great ability; but as it is, he has left his trace on the progress of chemistry by the careful work which he succeeded in accomplishing.

W. R.

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EDWARD CHARLES CORTIS STANFORD was born at Worthing on February 23rd, 1836, and was educated at All Saints' College, Maidstone, and at Craufurd College, Maidenhead. On leaving school, he became a pupil under his father, a pharmacist, at Worthing, where he enjoyed opportunities to develop the taste for chemistry which he had acquired during his school career. After a short course of practical chemistry under Redwood in the Pharmaceutical Society's laboratory, he was admitted a member of the Pharmaceutical Society in 1860. He held the teachership of chemistry in Worthing College for two years, lectured on chemistry and physics in Craufurd College for one year, and in 1862 was appointed assistant demonstrator in chemistry and

pharmacy in the Pharmaceutical Society's laboratory under Professor Redwood. In the same year, Stanford turned his attention to the economic applications of seaweed, and read a paper on the subject before the Society of Arts, for which he was awarded the Silver Medal of the society. This paper attracted the attention of the Duke of Argyll, and its author was eventually induced to take up his residence in Scotland with a view of developing the kelp industry. After a stay of eighteen months in the Outer Hebrides, where he studied the conditions of kelp manufacture, he established, with others, the British Seaweed Company's works at Whitcrock, eventually became managing director of the North British Chemical Company, and was connected with their works at Clydebank for upwards of thirty-five years.

Stanford's name is mainly associated with the development of the iodine and bromine industry in Scotland, and in general of the products to be obtained from algæ. He contributed various papers to scientific journals on the manufacture of iodine, and wrote the article on that subject in Thorpe's "Dictionary of Applied Chemistry." He was the author of papers on the action of charcoal on organic nitrogen and on algin in our Journal, and the Graham Gold Medal, given triennially for the best technical research in chemistry, was awarded to him in 1884 for the discovery of this substance, Stanford paid much attention to the sewage question, and contributed a number of papers to the Chemical Section of the Glasgow Philosophical Society, of which he was for a time president, on this subject. For some years, he was chairman of the School Board in Clydebank and was one of the governors of the Glasgow and West of Scotland Technical College.

He was a man of a happy, genial disposition, with a strong sense of humour, and possessed of many social gifts, which made him a welcome member of the annual conferences of the British Pharmaceutical Society, the British Association for the Advancement of Science, and the Society of Chemical Industry. He was elected a Fellow of the Chemical Society on April 21st, 1859, and died on December 8th, 1899.

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SIDNEY AUGUSTUS SWORN was born at Southampton in 1866 and was educated at the Hartley Institute of that town. In 1882, he obtained an exhibition at the Royal College of Science, Dublin, where he studied chemistry under Professor Hartley. He was elected in 1884 to the open Brackenbury Science Scholarship at Balliol College, Oxford, working under Professor H. B. Dixon until 1888, when he obtained a first class in the Final Honour Schools in chemistry. He began original work on the constitution of aromatic compounds while at Oxford, and on his appointment to a science mastership at

Cheltenham was able to continue his research, which was finally published in the *Philosophical Magazine* and the British Association Report for 1889. In the following year, he worked for a time with Professor T. E. Thorpe on persulphocyanogen. In 1893, he was appointed science master at the Gravesend Municipal Technical School. He began an investigation on the fixed points of mercurial thermometers, attempting to correlate the indications of standardised thermometers, made of different kinds of glass, with the absolute scale. An account of this work was read before the Royal Society in 1897.

He met with a bicycle accident in March, 1899, from the results of which he died a few weeks later. He was ardently devoted to experimental study, and by his death we lose one who could scarcely have failed to win distinction in the world of science. H. B. B.

WILLIAM THORP, B.Sc. (Lond.), whose recent death, at the comparatively early age of 53, will be felt as a serious loss to industrial chemistry, was a Londoner by birth and training. In 1857, he entered the City of London School, a school which had already undertaken for some years systematic instruction in Natural Science, and in this respect was a pioneer in scientific education. Under the genial and stimulating influence of the science master of that school, Thomas Hall, B.A., William Thorp was led to interest himself in chemistry, with the view of following it as a profession, and, like many others who came under Hall's influence, Thorp always spoke of his old master and school in terms of devoted affection. In 1864, he proceeded to the fuller study of chemistry and related branches of science at the Royal School of Mines and the Royal College of Chemistry, and was again fortunate in being brought into contact with A. W. Hofmann, who then filled the chair of chemistry. Frankland, who succeeded Hofmann in this chair, appointed Thorp to the position of Assistant Chemist to the Rivers Pollution Commission, on which Frankland was the chemist, and Thorp's important work in this direction only terminated with the conclusion of the Commission's labours in 1877. During his student days in the laboratory of the Royal College of Chemistry, Thorp had associated himself with two active investigators. With one of them, E. T. Chapman, he subsequently published the results of conjoint researches upon the extent to which a boiling alkaline solution of permanganate decomposes various organic substances. With the other, Capel Berger, he prosecuted investigations into the hydrolysis of starch and other carbohydrates at temperatures higher than 100°. The latter investigations were undertaken for industrial purposes and were not published. At the death of Capel Berger in 1872, Thorp was asked by the firm of Lewis Berger and

Co. to continue the chemical work of their deceased partner. When the Rivers Pollution Commission had completed their experimental work, Thorp was appointed chief chemist to this firm, in which he afterwards held the position of director, and latterly the position of consulting chemist. During his active connection with chemical manufacture, Thorp carried out much original work of the greatest value and was considered to be an expert in the chemistry of vermilion and of white lead. As a literary chemist, he worked with Groves in editing the technological volumes on Lighting and Gas-lighting; he also contributed the section of water analysis to Sutton's "Volumetric Analysis," whilst he rendered constant aid on the publication committee of the Society of Chemical Industry. Of the last-mentioned society he was an invaluable member, and had served as chairman of the London section and as Vice-President of the whole society. An original Fellow of the Institute of Chemistry, he advanced the interests of that Institute by his energetic, tactful, and judicious service on the Council, and, indeed, the councils of various associations of chemists have always placed much value on Thorp's assistance and advice.

William Thorp was elected a Fellow of the Chemical Society in 1866; he contributed to the Transactions and served on the Council of the Society, whilst few have preserved over so long a period a regular attendance at its meetings and have shown so great an interest in its procedure and success.

Those who knew Thorp and had broken through his natural reserve are unanimous in their esteem and affection for him. A man of absolutely unimpeachable honour, a sincere and unwavering friend, an indefatigable worker throughout a life of weak and broken health, one who made it a duty to show courtesy and kindly consideration to all, it is felt by those who knew him best that his loss will indeed be an irreparable one.

F. C.

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With JOHANN KARL FERDINAND TIEMANN, there passed away, on the 14th of November, 1899, one of those men whose memory will remain fresh with all who had the good fortune to be pupils of A. W. Hofmann during the period of his greatest activity at the University of Berlin.

Dr. Tiemann was born on the 10th of June, 1848, at Rübeland in the Harz. At his father's wish, he became apprentice to a druggist, but left in 1866 in order to study chemistry and pharmacy at the Collegium Carolinum—the present Technical High School—at Brunswick. In 1869, he proceeded to Berlin and entered Hofmann's laboratory. The marvellous influence which the great master exercised over all who came in contact with him was especially ex-

perienced by Tiemann. None of his pupils was so long and so intimately associated with Hofmann or appeared more anxious to adopt his characteristic manners and habits. With the exception of one year's absence whilst he served his country as a soldier in the Franco-German war, Tiemann was connected with the laboratory in the Georgenstrasse until Hofmann's death. In his capacity as laboratory assistant for twenty years, he gave instruction in practical chemistry to hundreds of the students who thronged to the school of Berlin from all parts of the world, and who, like the writer of this brief sketch, gratefully remember the valuable help and kind advice they received from him. Hofmann's striking personality and his astonishing faculty for making others work had a most stimulating effect on Tiemann. In 1878, he became a Privatdocent and four years afterwards was made Extraordinary Professor. His lectures on inorganic analysis and on a variety of subjects connected with organic chemistry, gave ample proof of his elocutionary ability and the great delight he took in lecturing. Besides the astonishing activity he displayed in teaching and in scientific investigation, he took for a long period an important part in the work of our sister Society in Berlin, fulfilling the double duties of Editor and Secretary. After holding the former office for fifteen years he resigned it in 1897, but remained Secretary until his death. The ability and tact he displayed during the tenure of these posts will be recognised by everyone who had to deal with him in his official capacity. In connection with the perfume industry, which was largely developed by his discoveries, he had occasion frequently to visit London, and this gave him opportunities of keeping up his acquaintance with English chemists. He became a Fellow of the Chemical Society in 1881.

Tiemann's work, although principally belonging to the field of organic chemistry, which he enriched by many brilliant discoveries, also dealt with chemical analysis. For many years he devoted himself to testing the various chemical methods for the examination of water, with the view of selecting those which allowed of the greatest simplicity in the necessary operations and apparatus, without impairing the accuracy of the results. This comparative study, besides forming the subject of Tiemann's earliest publications in the *Berichte*, is embodied in the revised edition of Kubel's treatise on water analysis, which he produced in 1874. Fifteen years later, he published, with Gaertner, the large handbook which treated of both the chemical and bacteriological examination of water.

The work, however, which stamped Tiemann as an original investigator of the highest order, as well as making his name known beyond the chemical world, was his synthetical preparation of vanillin. In the important research on coniferin, which he carried out with the assist-

ance of W. Haarmann, he showed that this glucoside yielded, on oxidation, the aromatic principle of vanilla. Tiemann elaborated a method for the quantitative determination of this substance in the bean, established its constitution, and ultimately made the manufacture of vanillin from coniferin possible. The application of Reimer's well-known method for the production of hydroxyaldehydes by the action of chloroform and potash on phenols, whilst affording a method of obtaining vanillin, supplied Tiemann at the same time with experimental material which, with the additional use of Perkin's reaction, led to our extensive knowledge of the whole group of substances related to protocatechuic acid and its isomerides.

The results arrived at by the study of coniferin induced him similarly to investigate other natural glucosides, such as hesperidin, daphnetin, and æsculetin, which he undertook in conjunction with Dr. Will and others. Hand in hand with these researches went the preparation of artificial glucosides by acting on the natural members of this group with acetaldehyde, or acetone in the presence of dilute alkali.

He also carried out a series of experiments upon the nitriles, the results of which formed the subject matter of a large number of doctor-theses for his pupils. This work led to a general method of formation of amido-acids, amidoximes, azoximes, and hydrazoximes.

The researches on glucosides, mentioned above, illustrate the predilection Tiemann had for the investigation of plant products. It was due to the influence of his friend, Prof. E. Baumann, that he also took up the study of substances occurring in the animal organism. They jointly determined, in 1879, the constitution of indoxylsulphuric acid which had been recognised previously by Baumann and Brieger as the indigo-forming constituent of animal urine.

Five years later there followed Tiemann's work on glucosamine, the base obtained by Ledderhose from chitin. Those who at the time worked in Hofmann's laboratory will remember the quantity of earthenware vessels filled with lobster shells which were required in this research for the preparation of glucosaminehydrochloride. Tiemann succeeded in establishing the relation of this base to grape sugar by transforming it into phenylglucosazone. By the action of nitric acid on glucosamine, he obtained isosaccharic acid; he repeatedly studied this acid in order to fix its constitution, and finally concluded that it was to be regarded as an hydrogenised furfuran derivative.

In 1893 there began the series of papers containing Tiemann's masterly researches on the terpenes and camphors which continuously occupied his attention until his death. The starting point of these investigations was the isolation and study of irone, the aromatic principle of the violet root, which was carried out by Tiemann in

conjunction with G. de Laire and P. Krüger, and culminated in the artificial preparation of the valuable perfume ionone. Then came in quick succession his researches on pinene and camphor, which led to the knowledge of a large number of new derivatives, and especially those of the limonene group. Prof. von Baeyer has summed up the importance of Tiemann's researches on this group by his statement that "with this work the chemistry of the limonene group is to be regarded as fully established."

In the above sketch, the writer has attempted as briefly as possible to give an account of Tiemann's scientific life work. His task has been rendered comparatively easy, as he was able to consult the excellent obituary notice of his late friend which Prof. Emil Fischer has recently published in the *Berichte*. S. R.

DR. DAVID WATSON was born on July 27th, 1846, in Kensington. He received his chemical education at the College of Chemistry in Oxford Street and at the Royal School of Mines in Jermyn Street, where he took his Associateship in metallurgy and geology in 1867. After obtaining his doctorate at the University of London, he became a teacher of chemistry at Chester College, but subsequently turned his attention to technology, and after holding appointments with Cammell and Co., of Sheffield, and with Sir Lowthian Bell at Washington, he became chemist, and afterwards manager, of the Broughton Copper Works, Manchester. He was elected into the Chemical Society on January 18th, 1872, and at the time of his death, December 15th, 1899, was chairman of the Manchester section of the Society of Chemical Industry.

### L.—*Electrolysis of the Nitrogen Hydrides and of Hydroxylamine.*

By EMERIQUE CHARLES SZARVASY, Ph.D.

THE present communication forms part of a comprehensive research I have undertaken in order to examine the behaviour of nitrogen compounds under the influence of the electric current, and therefore only a short account of the experimental facts will be given, leaving general considerations to a future occasion.

The electrolyses of ammonia, hydrazine, azoimide, hydroxylamine, and their salts were carried out at different current densities, tem-

peratures, and concentrations, and the conditions were determined under which, by electrolytic decomposition, ammonia, hydrazine, or azoimide yields its two components in the proportion contained in the molecule.

The experiments were carried out in an apparatus which admitted of the gases liberated at the two electrodes being collected and measured separately. An adjustable resistance ampèremeter, a copper and a gas voltmeter were in the circuit, and a voltmeter in shunt.

### *Ammonia.*

Solutions of ammonia and its mixtures with sodium chloride were electrolysed by Losanitsch and Jovitschitsch (*Ber.*, 1896, 29, 2436), who found that secondary reactions almost invariably take place, the nitrogen liberated at the anode being less than that required by the proportion  $N_2:3H_2$ . An exceptional case occurs when the mixture  $9NaCl:NH_3$  is electrolysed at  $100^\circ$ ; the gases are then liberated in the proportion  $N_2:3H_2$ , and no secondary products are formed.

My experiments (Table I.) show that if sufficiently high current densities are employed, ammonium hydroxide, either alone or mixed with sodium chloride, on electrolysis even at the ordinary temperature, yields its two component elements in the proportion contained in the molecule, unaccompanied by secondary reactions; only traces of nitrites and nitrates could be detected in the electrolysed liquid.

TABLE I.

Exp.	Solution.	$D_a$ .	$D_c$ .	c.c. at $0^\circ$ and 760 mm.		Temp.
				Nitrogen.	Hydrogen.	
1	20 per cent. ammonia...	352.1	352.1	5.6	16.9	$20.1^\circ$
2	" "	246.5	246.5	10.2	30.8	22.2
3	" "	153.6	153.6	11.7	35.5	21.7
4	" "	156.8	156.8	9.7	29.2	98.9
5	10 per cent. ammonia, 20 per cent. NaCl	301.8	301.8	4.7	14.2	21.5
6	" "	260.1	260.1	6.6	20.1	22.4
7	" "	211.8	211.8	8.1	24.5	22.2
8	" "	148.7	148.7	11.4	34.4	21.7
9	" "	147.1	147.1	7.8	23.5	99.3

In the columns  $D_a$  and  $D_c$  respectively, the current densities on the anode and cathode are given, the numbers being calculated in ampères per square decimetre of electrode surface,



*Hydrazine.*

Solutions of the base in water, containing the hydrazine hydrate, are very bad conductors of electricity.

TABLE II.

Exp.	Solution.	$D_{25}$	$D_c$	c.c. at 0° and 760 mm.		Temp.
				Nitrogen.	Hydrogen.	
1	50 per cent. of hydrazine	20.2	20.2	3.7	7.4	22.2°
2	" "	50.6	50.6	4.4	8.8	21.7
3	" "	117.7	117.7	4.7	9.4	23.8
4	" "	20.7	20.7	9.2	18.4	99.3
5	" "	52.1	52.1	6.1	12.2	99.6
6	" "	110.2	110.2	4.3	8.6	99.1
7	25 per cent. of hydrazine	21.7	21.7	6.7	13.4	22.2
8	" "	48.8	48.8	6.6	13.2	23.4
9	" "	120.1	120.1	5.3	10.6	25.1
10	" "	119.2	119.2	8.1	16.2	98.7
11	12 per cent. of hydrazine	19.3	19.3	12.2	24.4	22.1
12	" "	56.4	56.4	7.3	14.6	22.4
13	" "	118.1	118.1	6.1	12.2	25.3
14	" "	116.2	116.1	5.4	10.8	99.2

From this table, it can be seen that the hydrazine is resolved by the electric current into  $N_2:2H_2$ , and that this proportion remains unchanged, however much the experimental conditions are varied. The reaction may be explained by assuming that the hydrazine hydrate is ionised by the current, the two hydroxyls being carried to the anode, forming 1 molecule of water and evolving 1 atom of oxygen, which oxidises the hydrazine to water, nitrogen being liberated. On the cathode, the free base reacts with 2 mols. of water, the hydrate being reformed and hydrogen liberated.

The sulphate and chloride of hydrazine were also electrolysed; the results are given in Table III (p. 606).

When collected and examined, the gases were found to be pure nitrogen at the anode, and pure hydrogen at the cathode. No secondary products were detected in the electrolysed liquid. The chlorine liberated on the anode reacts with the hydrazine, forming hydrochloric acid with liberation of nitrogen. An analogous reaction takes place when hydrazine sulphate is electrolysed; it is remarkable that no trace of the oxidation products of nitrogen could be detected in the liquid.

TABLE III.

Exp.	Solution.	$D_a = D_c$ .	c.c. at 0° and 760 mm.		Temp.
			Nitrogen.	Hydrogen.	
1	25 per cent. chloride.....	25.1	2.2	4.4	22.1°
2	" " .....	30.0	3.1	6.3	98.6
3	" " .....	116.4	3.4	6.8	22.3
4	" " .....	150.6	2.7	5.5	98.9
5	10 per cent. chloride.....	30.6	3.9	7.8	21.5
6	" " .....	122.3	2.7	5.4	22.3
7	3 per cent. sulphate .....	22.1	2.3	4.6	21.4
8	" " .....	156.7	3.1	6.2	21.7
9	About 35 per cent. sulphate .....	20.3	5.3	10.6	99
10	" " .....	164.1	7.2	14.4	99

*Azoimide.*

Before proceeding to a description of the experiments with azoimide, some details may be given concerning the preparation of this compound in considerable quantities, as this has always been considered a rather difficult and dangerous operation.

With the exception of that of Wislicenus, the methods of different authors were found to give very poor yields; Wislicenus' method, if a suitable apparatus is employed, allows of the preparation of azoimide on a large scale with comparative ease.

The apparatus I used was a circular, thick-walled cast iron vessel with a straight iron outlet tube screwed in the shoulder at an angle of about 45°. The mouth of the vessel was closed by an iron plug which screwed down closely on an inner ledge, giving a gas-tight joint. An iron leading tube was fitted through the plug reaching nearly to the bottom of the vessel. The wall of the vessel was drilled with a vertical tube to carry a thermometer. The dimensions of the apparatus were such that 50 grams of sodium could be worked with in one operation. This amount was converted into the amide at a temperature of 360—390°. The amide was then converted into sodium azoimide by passing nitrous oxide over the fused product. For this part of the process the most favourable temperature was found to be from 190—220°. A yield of as much as 56 per cent. of the theoretical amount was obtained, this being about 6 per cent. higher than that recorded by Wislicenus. It was surprising to find cyanide in the product, the only possible explanation being that the iron contained carbon which, at about 400°, in presence of sodium, reacted with the ammonia, forming sodium cyanide. The best way

to eliminate this impurity is to precipitate the crude sodium azoimide with alcohol, the sodium cyanide remaining in solution.

In the following table, the results of the electrolysis of the acid and its sodium salt are formulated :

TABLE IV.

Exp.	Solution.	$D_a$	$D_c$	c.c. at 0° and 760 mm.		Temp.
				Nitrogen.	Hydrogen.	
1	20 per cent. azoimide...	270	270	33.1	11.1	15°
2	" "	150	150	22.3	7.5	"
3	" "	112	112	25.2	8.5	"
4	" "	85	85	27.4	9.2	"
5	32.5 per cent. sodium salt	281.2	140.6	70.35	23.6	20
6	" "	162.5	81.2	86.40	29.4	"
7	" "	162.5	81.2	85.8	29.4	"
8	" "	119	59.5	88.8	30.45	"
9	" "	56.2	112.5	77.2	25.6	"
10	" "	462.5	231.2	78.2	26.2	"
11	40 per cent. sodium salt	250	125	39.3	13.21	10-12
12	" "	438	219	40.0	13.4	8-9
13	" "	182	91	39.6	13.35	10-12
14	" "	188	94	38.8	13.1	13-14
15	" "	115.6	51.8	39.18	13.2	6-10
16	20 per cent. sodium salt	112.5	56.2	39.21	13.3	10
17	" "	112.5	56.2	39.4	13.3	10
18	" "	250	125	39.18	13.21	10-15
19	32 per cent. sodium salt	100	100	48.2	16.2	24
20	" "	165.6	165.6	39.6	13.1	24
21	" "	168.7	168.7	21.4	7.3	24
22	" "	259.4	259.4	31.2	10.6	30
23	" "	275	275	34.9	28.3	40

Slight traces of ammonia, but no oxidation products of nitrogen, were found in the electrolysed liquid. In some of the experiments, the ratio of hydrogen to nitrogen was found to be less than that required by the expression  $H_2 : 3N_2$ . The deficiency of nitrogen seemed to indicate that some condensation of this element to a polymeride of the type  $N_3$  or  $N_6$  had taken place on the anode during the electrolysis. In order to test this possibility, density determinations of the gas evolved under two sets of conditions were made, but in each case the values obtained proved it to be pure nitrogen.

As an extension of these experiments, it is my intention to electrolyse mixtures of azoimide with its salts at very high current densities and low temperatures, thereby hoping to effect a condensation of nitrogen in a process which is analogous to that in which percarbonates and persulphates are produced.

*Hydroxylamine.*

I have made several attempts to electrolyse the base, but failed owing to the difficulty of preventing the spontaneous transformation of hydroxylamine into ammonia.

Solutions of the sulphate of this base were electrolysed under varying conditions; the results show that secondary reactions always take place, the base being reduced on the cathode to ammonia and oxidised at the anode to oxygen compounds of nitrogen. Under certain conditions, the whole of the hydrogen is absorbed in the reaction.

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# LI.—*Constitution of Amarine, of its supposed Dialkyl- and Diacyl-derivatives, and of Isoamarine.*

BY FRANCIS R. JAPP, F.R.S., and JAMES MOIR, M.A., B.Sc.

By the action of potassium hydroxide on dialkylamaronium\* halides, various bases have been obtained, to which their discoverers have ascribed the constitution of dialkylamarines. Thus Claus and Elbs (*Ber.*, 1880, 13, 1419) prepared compounds which they regarded as dimethylamarine,  $C_{21}H_{18}(CH_3)_2N_2$  (m. p.  $146^\circ$ ), and dibenzylamarine,  $C_{21}H_{18}(C_7H_7)_2N_2$  (m. p.  $139-140^\circ$ ). They state that these bases unite with hydracids to form salts isomeric with the original quaternary halides, but differing from them in being instantaneously decomposed by ammonia, even in the cold.

Borodin (*Annalen*, 1859, 110, 83) had previously obtained, in like manner, a base which he formulated as diethylamarine,  $C_{21}H_{18}(C_2H_5)_2N_2$  (m. p.  $110-115^\circ$ ).

We have re-investigated these three bases and can confirm the statements of the discoverers as to the physical properties of the compounds, except that Borodin's "diethylamarine" melts, when pure, at  $125^\circ$ ; but we find that the bases have the composition of *dialkylamarines* plus the elements of a molecule of water. Thus

So-called dimethylamarine is  $C_{21}H_{18}(CH_3)_2ON_2$ .  
 „ diethylamarine „  $C_{21}H_{18}(C_2H_5)_2ON_2$ .  
 „ dibenzylamarine „  $C_{21}H_{18}(C_7H_7)_2ON_2$ .

These bases do not part with water on heating. Moreover, they unite with acids without eliminating water, so that, contrary to Claus

\* We adopt Victor Meyer's suggestion (*Ber.*, 1894, 27, 505) that the names of all quaternary ammonium radicles and their analogues should end in "onium."

and Elbs's statement, the salts are not isomeric with the corresponding dialkylamaronium salts.

It is worthy of note that Claus (*Ber.*, 1882, 15, 2326), by the action of benzylic chloride on "dimethylamarine," obtained compounds containing the elements of a molecule of water more than he had anticipated. He regards these compounds as derivatives of "hydroamarine,"  $C_{21}H_{20}ON_2$ , and assumes that the water came from the alcohol employed as a solvent in the reaction. In reality, the elements of water were present to start with in the "dimethylamarine."

We have made a detailed study of the so-called dibenzylamarine (m. p. 139—140°) and have arrived at the conclusion that it is *benzoyl-s-*

*dibenzyl-i-diphenylethylenediamine*,  

$$\begin{array}{c} C_6H_5 \cdot CH \cdot N(C_7H_7) \cdot CO \cdot C_6H_5 \\ C_6H_5 \cdot CH \cdot NH \cdot C_7H_7 \end{array}$$

As the stereoisomeric *s*-diphenylethylenediamines (stilbenediamines) play an important part in this research, it is necessary to indicate briefly the present state of our knowledge of these compounds, the more so as the literature of the subject is in a somewhat confused state.

*i*-Diphenylethylenediamine (*i*-stilbenediamine), m. p. 120—121°, was obtained by Grossmann (*Ber.*, 1899, 22, 2298) by reducing amarine in boiling alcoholic solution with sodium and hydrolysing the resulting dibenzylidene-*i*-diphenylethylenediamine with acids. It proved to be identical with a base of previously unknown constitution obtained by Müller and Limpricht by the action of ammonia on benzaldehyde containing hydrocyanic acid (*Annalen*, 1859, 111, 141). Grossmann does not state that his base is the meso-, or true inactive, form, as at that time it was the only form known.

The stereoisomeric *r*-diphenylethylenediamine (m. p. 90—92°) was obtained by Feist (*Ber.*, 1894, 27, 214) by the reduction of either  $\alpha$ - or  $\beta$ -benzildioxime, and was afterwards resolved into its optically active constituents by Feist and Arnstein\* (*Ber.*, 1895, 28, 3169). Feist appears to have been unacquainted with Grossmann's work—at least he does not refer to it. In Beilstein's *Handbuch*, 3rd ed., 4, 978, and in M. M. Richter's *Lexikon der Kohlenstoff-Verbindungen*, p. 1397, Grossmann's base and Feist's base figure as one and the same substance.

We have examined the two bases and find them quite distinct.

We endeavoured to obtain independent evidence of the configuration of Grossmann's base by converting it, by the action of nitrous acid, into the corresponding  $\alpha\beta$ -diphenylglycol. The expected hydrobenzoin was

\* We follow Feist and Arnstein's practice in referring to this base as racemic, although, for anything these authors show to the contrary, it may, like isohydrobenzoin, with which it corresponds, be a mere externally compensated mixture of the two enantiomorphs.

obtained, but apparently mixed with a little isohydrobenzoin. Moreover, isodiphenylhydroxethylamine was formed as an intermediate product, instead of the expected diphenylhydroxethylamine. These results, as we show later, indicate the occurrence of a migration, so that no direct conclusion can safely be drawn from them as to the configuration of Grossmann's base. But they confirm the view that this base is an  $\alpha\beta$ -diphenylethylenediamine, and it must therefore be the meso-form, inasmuch as Feist's stereoisomeric base has been resolved into the dextro- and lævo-forms.

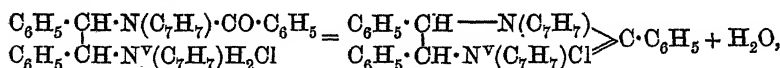
The chief result of the present investigation is to show that amarine and its supposed dialkyl compounds are derived from Grossmann's  $\alpha\beta$ -diphenylethylenediamine, whilst Snape and Brooke's isoamarine is the corresponding racemic (or, possibly, only  $[d+l]$ -) form, derived from Feist's  $\alpha$ -diphenylethylenediamine.

By reducing dibenzylidene- $\alpha$ -diphenylethylenediamine with sodium in alcohol, Grossmann (*loc. cit.*, 2301) obtained  $s$ -dibenzyl- $\alpha$ -diphenylethylenediamine,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$  (m. p.  $153^\circ$ ). We have confirmed the symmetrical structure of this compound by preparing from it a *dinitroso*-compound (needles, melting at  $233^\circ$ ).

By acting with benzoic chloride on  $s$ -dibenzyl- $\alpha$ -diphenylethylenediamine, we obtained, as chief product, a *dibenzoyl* derivative,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N}(\text{C}_7\text{H}_7) \cdot \text{CO} \cdot \text{C}_6\text{H}_5$  (m. p.  $268^\circ$ ), and in smaller quantity, a *monobenzoyl* derivative,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N}(\text{C}_7\text{H}_7) \cdot \text{CO} \cdot \text{C}_6\text{H}_5$  (m. p.  $139.5^\circ$ ), the latter being identical with Claus and Elbs's so-called dibenzylamarine, the true constitution of which was thus rendered clear. This constitution was confirmed by the observation that Claus and Elbs's "dibenzylamarine," prepared from dibenzylamaronium chloride, yields, when heated with benzoic chloride, a monobenzoyl derivative (m. p.  $268^\circ$ ) identical with the foregoing dibenzoyl- $s$ -dibenzyl- $\alpha$ -diphenylethylenediamine.

Judging from the analogy of the so-called dibenzylamarine, Claus and Elbs's so-called dimethylamarine (m. p.  $146^\circ$ ) is *benzoyl-s-dimethyl- $\alpha$ -diphenylethylenediamine*,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N}(\text{CH}_3) \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ ; Borodin's so-called diethylamarine is the corresponding *diethyl* derivative,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N}(\text{C}_2\text{H}_5) \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ ; and the other so-called dialkylamarines—thus "ethylbenzylamarine"—described by Claus and his pupils will doubtless have to undergo similar modifications both of composition and of constitution.

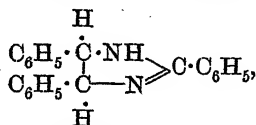
We find that when monobenzoyl-*s*-dibenzyl-*i*-diphenylethylenediamine hydrochloride is heated to 220°, it parts with the elements of water, yielding dibenzylamaronium chloride:



a reaction which proves conclusively the constitution of the dialkylamaronium salts. An analogous change occurs with the salts of other acids.

In like manner, benzoyl-*s*-dimethyl-*i*-diphenylethylenediamine hydriodide ("dimethylamarine" hydriodide) parts with the elements of water when heated, yielding dimethylamaronium iodide, the reaction in this case taking place, although slowly, even on boiling an aqueous solution of the salt containing free hydriodic acid.

Amarine is therefore 2-phenyl-4 : 5-*cis*-diphenyl-4 : 5-dihydroimidazole,

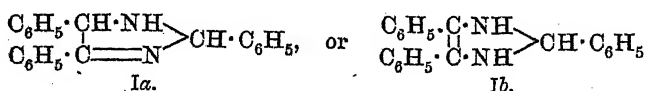


I. *cis*-Modification (*meso*).

employing the numbering of the imidazole ring  $\begin{array}{c} \text{NH} \\ \text{5} \quad \text{1} \\ \text{4} \quad \text{2} \\ \text{N} \end{array}$  adopted by M. M.

Richter in his *Lexikon der Kohlenstoff-Verbindungen*. A formula structurally identical with the foregoing, but in which the configuration was not indicated, was put forward by Claus (*Ber.*, 1882, 15, 2333).

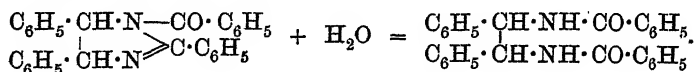
Two further formulæ for amarine were suggested by Emil Fischer : either



(*Annalen*, 1882, 211, 217). The latter formula was also proposed independently by Japp and Robinson (*Trans.*, 1882, 41, 329). It is to be noted that these two formulæ are tautomeric modifications of Formula I—Ia being an intermediate stage in the transformation of I into Ib.

It appeared possible that Bahrmann's diacetylamarine (*J. pr. Chem.*, 1883, [ii], 27, 298) and Claus and Scherbel's dibenzoylamarine (*Ber.*, 1885, 18, 3083) might be derived from the di-imino-form Ib. We find, however, that neither of these compounds has the constitution—or even the composition—assigned to it. The supposed dibenzoylamarine proves to be identical with Grossmann's *s*-dibenzoyl-*i*-diphenylethylene-

diamine,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$  (*loc. cit.*, 2300), whilst the supposed diacetylamarine is the corresponding *acetylbenzoyl-i-diphenylethylene-diamine*,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3$ . These compounds are obtained by acting on amarine with acid chlorides and boiling the product with alcohol. A monacylamarine is probably first formed, and then takes up the elements of water, the dihydroimidazole ring opening up in the process, just as in the formation of the supposed dialkyl-amarines. In confirmation of this view, we find that monobenzoylamarine, when warmed with acids in alcoholic solution, is speedily transformed into *s-dibenzoyl-i-diphenylethylenediamine*,



We have not examined Bahrman's "dicarbethoxylamarine," which he obtained by the successive action of ethylic chlorocarbonate and alcohol on amarine (*loc. cit.*, 303), but we would point out that his analytical results agree better with the formula of a *benzoylcarbethoxyl-i-diphenylethylenediamine*,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{CO}_2\text{C}_2\text{H}_5$ , than with that which he deduces.\* This would bring it into line with the two preceding compounds, and all evidence in support of the di-imino-formula for amarine would be thus withdrawn.

On account of the *cis*-position of the 4:5-phenyl groups, amarine is a meso-compound and ought not to exist in optically active forms. The asymmetry of its formula, dependent on the presence of a hydrogen atom in position 1, is only an apparent asymmetry, as this hydrogen atom may oscillate, by tautomeric change, between positions 1 and 3 (compare v. Pechmann, *Ber.*, 1895, 28, 876). The 1-monalkylamarines would, however, probably be separable into optically active isomerides.

There ought, however, to be a stereoisomeric amarine in which the 4:5-phenyl groups are in the *trans*-position, and which would therefore exist in optically active forms. This compound is easily obtained. We find that when amarine is fused, 8 per cent. of sodium added, and the temperature raised to 190—200°, the whole solidifies, owing to the formation of a sodium compound of Snape and Brooke's isoamarine (*Trans.*, 1899, 75, 208), from which an excellent yield of the free base may be obtained. Isoamarine may also be prepared by heating amarine hydrochloride for a short time at a temperature a few

\* Bahrman finds C=73.63, 73.83; H=6.31, 6.26; N=7.01 per cent. The formula proposed by us,  $\text{C}_{24}\text{H}_{24}\text{O}_2\text{N}_2$ , requires C=74.22; H=6.18; N=7.22; Bahrman's formula,  $\text{C}_{27}\text{H}_{26}\text{O}_2\text{N}_2$ , would require C=73.30; H=5.88; N=6.24 per cent.

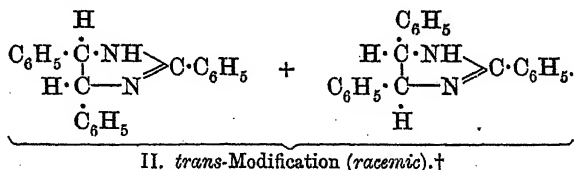


degrees above its melting point, when it is for the most part converted into isoamarine hydrochloride. A little lophine is simultaneously formed in both reactions, but, in the case of the hydrochloride, this may be almost completely prevented by carrying out the heating in an atmosphere of gaseous hydrogen chloride.

Suspecting isoamarine to be the racemic form of amarine, we made, with Professor Snape's permission, some experiments to test the correctness of this supposition. In the first place, however, an ebullioscopic determination of the molecular weight showed that isoamarine is isomeric—not polymeric—with amarine.

Isoamarine was then reduced with sodium in boiling alcoholic solution. As in Grossmann's analogous experiment with ordinary amarine, a benzylidene derivative was obtained, which, on hydrolysis with acids, yielded a base—in the present case, Feist's *r*-diphenylethylenediamine. This shows that isoamarine is related to the latter base in the same way as amarine to Grossmann's *i*-diphenylethylenediamine. This conclusion was confirmed by the fact that Feist's base (prepared by the reduction of  $\alpha$ -benzildioxime), when heated with benzoic acid at 170–180°, yielded isoamarine. Amarine benzoate, heated at the same temperature, undergoes no change, showing that isoamarine is the primary product in the foregoing synthesis.

Isoamarine is therefore the racemic form\* of amarine. It is a combination of the two opposite optically active forms of 2-phenyl-4:5-trans-diphenyl-4:5-dihydroimidazole,



The possibility of tautomeric oscillation of the hydrogen atom of the imino-group between the two nitrogen atoms points to the existence of only one pair of enantiomorphs. In the case of the 1-monalkyl-isoamarines, there should be two pairs.

Feist and Arnstein (*Ber.*, 1895, 28, 3177) state that by heating  $\alpha$ -dibenzoyl-*r*-diphenylethylenediamine in a current of gaseous hydrogen chloride, they obtained an isomeride of amarine melting at 175°. We have repeated this experiment and find that the compound in reality melts at 198°, and is in all respects identical with Snape and Brooke's isoamarine.

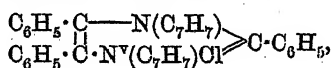
\* Or, possibly, only the [*d*+*l*]-form.

† Since the publication of our preliminary note on this subject (*Proc.*, 1899, 15, 212), Snape has announced (*Proc.*, 1899, 15, 228) that he has succeeded in resolving isoamarine, by means of tartaric acid, into its enantiomorphs.

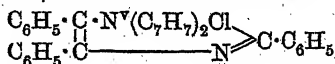
The earliest preparation of this compound, however, dates much further back. We find that the base which Ekman (*Annalen*, 1859, 112, 169) obtained, along with other products, by heating dry hydrobenzamide hydrochloride, and which, according to him, has the melting point  $200^{\circ}$  and the formula  $C_{21}H_{20}N_2$  is in reality isoamarine,  $C_{21}H_{18}N_2$ . In this reaction, amarine hydrochloride is doubtless first formed, and is then changed, by the further action of heat, into isoamarine hydrochloride, as in the reaction described by us.

We leave the further investigation of isoamarine to Professor Snape, and are greatly indebted to him for allowing us to pursue the subject so far.

Dibenzylamaronium chloride yields a stable, crystalline dichromate of the formula  $(C_{85}H_{31}N_2Cl)_2 \cdot H_2Cr_2O_7$  (m. p.  $173^{\circ}$ ), which may be boiled with glacial acetic acid without undergoing decomposition. If, however, a little strong hydrochloric acid is added to the solution in glacial acetic acid and the mixture boiled, the chromic acid is reduced, and *dibenzyllophonium chloride* is formed. This mode of formation shows that the latter substance has the constitution



instead of, as suggested by Japp and Davidson,



(*Trans.*, 1895, 67, 33). In the formation of quaternary halides from imidazoles and alkyl halides, the iminic hydrogen is, therefore, first replaced by alkyl, after which the alkyl halide unites with the other nitrogen atom—that is, with that which was tertiary from the beginning. This has recently been proved in a totally different way by Pinnow and Sämann (*Ber.*, 1899, 32, 2181). The mechanism of the formation of the dialkylamaronium halides from amarine and alkyl halides is identical with this.

We incline to the view that the so-called dibenzyllophonium hydroxide (Japp and Davidson, *loc. cit.*) has either the constitution  $C_6H_5 \cdot C \cdot N(C_7H_7) \cdot CO \cdot C_6H_5$ ,  $C_6H_5 \cdot C \cdot NH \cdot C_7H_7$ , corresponding with that of the analogous

amarine derivative, or  $\begin{array}{c} C_6H_5 \cdot C \cdot N(C_7H_7) \\ | \\ C_6H_5 \cdot C \cdot N(C_7H_7) \end{array} \rightarrow C(OH) \cdot C_6H_5$ , the latter being the carbinol formula proposed by Niementowski (*Ber.*, 1887, 20, 1888) for this class of pseudo-ammonium bases. Its solubility in water is quite out of keeping with the constitution of a true amarine hydroxide hitherto assigned to it. In contact with acids it parts with water, yielding a dibenzyllophonium salt of the

formula already given, the halogen or acid group attaching itself to nitrogen.

Various other results which were obtained in the study of "dibenzylamarine,"  $C_{21}H_{18}(C_7H_7)_2ON_2$ , and which in part led us to make the experiments already referred to, are described in the experimental portion of this paper. They entirely support the views here put forward as to its constitution.

## I. THE DIALKYLAMARONIUM SALTS AND THE SUPPOSED DIALKYLAMARINES.

### A. Dibenzyl Derivatives.

*Dibenzylamaronium Chloride* (*Benzylamarinebenzylic Chloride*),  $C_6H_5 \cdot CH-N(C_7H_7)$   
 $C_6H_5 \cdot CH \cdot N^+(C_7H_7)Cl \rightleftharpoons C \cdot C_6H_5$ .—The method of preparation described by Claus and Elbs (*Ber.*, 1880, 13, 1420) was followed, but the process of purification was modified.

A solution of 50 grams of amarine and 30 grams of benzylic chloride in 150 c.c. of alcohol was boiled for 12 hours, using a reflux condenser. On cooling, amarine hydrochloride\* separated in large, six-sided plates. The mother liquor from these was evaporated to dryness, and the residue extracted with a small quantity of boiling acetone, which readily dissolved the quaternary chloride, leaving behind any amarine hydrochloride; on expelling the acetone, the quaternary salt remained as a resinous mass. In this form it was used for the various experiments about to be described; but by cautiously adding strong hydrochloric acid to its cold saturated aqueous solution, it may be obtained in small, clear prisms, melting at  $49-52^\circ$  ( $40-75^\circ$ , Claus and Elbs;  $45^\circ$ , Claus and Kohlstock). Contrary to the statement of previous investigators, it is decomposed by ammonia, but only by long heating with alcoholic ammonia at  $100^\circ$ ; it thus yields the so-called dibenzylamarine (m. p.  $139^\circ$ ).

Various other dibenzylamaronium salts were prepared for the purpose of comparing them with substances formed in other reactions (*vide infra*). They are readily obtained by double decomposition of dibenzylamaronium chloride, in alcoholic solution, with the silver salt of the required acid.

*Nitrate*,  $C_{21}H_{17}(C_7H_7)_2N_2 \cdot NO_3$ .—Crystallises from benzene in thin, lustrous, rectangular laminae, melting at  $157-158^\circ$ . Very soluble in

\* Incidentally, we prepared and analysed amarine platinichloride. It crystallises from dilute alcohol in microscopic, oblique laminae of the formula  $(C_{21}H_{18}N_2)_2, H_2PtCl_6, 2H_2O$ .

It has been hitherto represented as anhydrous.

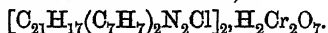
alcohol. An analysis of a specimen of this salt, obtained by a different reaction, is given later on.

*Acetate.*—Oblique prisms, melting, not sharply, at  $134^{\circ}$ . Not analysed.

The *nitrite* and the *benzoate* are gums, and were not analysed.

The foregoing salts, like the chloride, are decomposed by potassium hydroxide, but are unaffected by ammonia in the cold.

*Dibenzylamaronium chloride dichromate,\**



—This peculiarly constituted salt was obtained in the course of an attempt to oxidise dibenzylamaronium chloride. 10 grams of the latter compound were dissolved in glacial acetic acid, and 2 grams of chromium trioxide, in the same solvent, were added to the hot solution. No oxidation took place; and on cooling, orange-coloured tabular crystals, somewhat like potassium dichromate in appearance, were deposited. They were recrystallised from boiling glacial acetic acid. They melted at  $173^{\circ}$ , evolving benzylic chloride and leaving benzyllophine (m. p.  $165^{\circ}$ ), mixed with reduced chromium compounds. Analysis gave the following figures :

0.5538 gave 0.0690  $Cr_2O_3$ . Cr = 8.53.

1.0787 „ 0.1351  $Cr_2O_3$ . Cr = 8.57.

0.9019 „ 0.2067 AgCl. Cl = 5.67.

0.7035 „ 0.1638 AgCl. Cl = 5.74.

$[C_{21}H_{17}(C_7H_7)_2N_2Cl]_2, H_2Cr_2O_7$  requires Cr = 8.34 ; Cl = 5.69 per cent.

In this salt, the chromic acid is in combination with the tertiary nitrogen atom of the dibenzylamaronium chloride, and may be removed by ammonia in the cold. By dissolving the salt in cold alcoholic ammonia, adding water, and extracting the liberated dibenzylamaronium chloride with chloroform, the latter salt may be obtained in a state of great purity. It remains as a colourless gum on evaporating the chloroform, but may be made to crystallise by the method already described.

*Oxidation of Dibenzylamaronium Chloride to Dibenzyllophonium Chloride.*—As already mentioned, dibenzylamaronium chloride dichromate may be boiled with glacial acetic acid without undergoing chemical change. If, however, hydrochloric acid is added, oxidation takes place and the lophonium derivative is formed. Doubtless it is the liberated chlorine which withdraws hydrogen.

5 grams of dibenzylamaronium chloride dichromate were boiled with a quantity of glacial acetic acid insufficient to dissolve the whole, and a few drops of fuming hydrochloric acid was added, and the boiling continued.

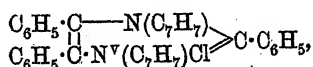
It is suggested to avoid using the name "chloro-dichromate," as it might suggest a compound analogous to that of the chlorochromates.

for 10 minutes, when all dissolved and the chromium trioxide was reduced. On diluting with water, dibenzyllophonium chloride separated, recognisable by its characteristic crystalline form and its melting point (253°). The platinichloride showed under the microscope the characteristic four- and six-pointed twin crystals (Trans., 1895, 67, 37).

0.7897 gave 0.1110 Pt.  $Pt = 14.06$ .

$[C_{21}H_{15}(C_7H_7)_2N_2Cl]_2 \cdot PtCl_4$  requires  $Pt = 14.32$  per cent.

Dibenzyllophonium chloride has, therefore, the constitution



starting from the constitution of dibenzylamaronium chloride proved in the present paper.

*Claus and Elbs's "Dibenzylamarine."*—By warming dibenzylamaronium chloride with alcoholic potassium hydroxide, as described by Claus and Elbs (*loc. cit.*), it is decomposed. We can confirm their statements as to the physical properties of the resulting compound, which crystallises from alcohol in slender, felted needles, or in rosettes, melting at 139°. Analysis, however, gave figures differing considerably from those required for dibenzylamarine, but agreeing well with the composition of *dibenzylamarine plus a molecule of water*,  $C_{35}H_{32}ON_2$ .

0.1638 gave 0.5076  $CO_2$  and 0.0963  $H_2O$ .  $C = 84.52$ ;  $H = 6.53$ .

0.1643 „ 0.5077  $CO_2$  „ 0.0971  $H_2O$ .  $C = 84.27$ ;  $H = 6.57$ .

0.1527 „ 0.4742  $CO_2$  „ 0.0965  $H_2O$ .  $C = 84.70$ ;  $H = 7.02$ .

0.1552 „ 0.4803  $CO_2$  „ 0.0926  $H_2O$ .  $C = 84.40$ ;  $H = 6.62$ .\*

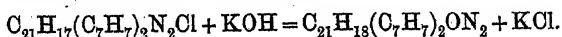
0.4561 „ 22.35 c.c. moist nitrogen at 14° and 769 mm.  $N = 5.72$

0.4042 „ 19.05 c.c. „ „ 14° „ 773 mm.  $N = 5.64$ .

$C_{35}H_{32}ON_2$  requires  $C = 84.68$ ;  $H = 6.45$ ;  $N = 5.64$  per cent.

No analysis of this substance is given in Claus and Elbs's paper; but Elbs (*Inaugural-Dissertation, Freiburg i. B.*, 1881, p. 21) gives a single combustion, the results of which— $C = 87.78$ ,  $H = 6.50$ —agree with the composition of dibenzylamarine,  $C_{35}H_{30}N_2$ . Required:  $C = 87.86$ ,  $H = 6.27$  per cent. He did not determine the nitrogen.

It is evident, however, from our analyses, that the compound has the formula  $C_{35}H_{32}ON_2$ , and that it is formed from dibenzylamaronium chloride according to the equation



It does not contain water of crystallisation, as it does not lose

\* Combustion IV was made by Mr. Alexander Findlay with a specimen of the substance again crystallised from alcohol.

weight on heating at 120°. We show, later on, that it is *benzoyl-s-dibenzyl-i-diphenylethylenediamine*,

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N}(\text{C}_7\text{H}_7) \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{C}_7\text{H}_7 \end{array}$$

It unites directly with acids to form salts, which, therefore, contrary to Claus and Elbs's statement, are not isomeric with the corresponding dibenzylamaronium salts, into which, however, they are transformed, with elimination of water, on heating. Owing to the occurrence of this change, their melting points are somewhat uncertain. As stated by Claus and Elbs, ammonia instantaneously decomposes them, even in the cold. They are best prepared in alcoholic solution.

*Hydrochloride*,  $\text{C}_{21}\text{H}_{18}(\text{C}_7\text{H}_7)_2\text{ON}_2\text{HCl}$ .—Colourless prisms, melting at 188° (197—199°, Claus and Elbs), readily soluble in alcohol, sparingly in water.

0.7540 gave 0.1985 AgCl. Cl = 6.51.

$\text{C}_{21}\text{H}_{18}(\text{C}_7\text{H}_7)_2\text{ON}_2\text{HCl}$  requires Cl = 6.66 per cent.

Claus and Elbs's formula,  $\text{C}_{21}\text{H}_{16}(\text{C}_7\text{H}_7)_2\text{N}_2\text{HCl}$ , on the other hand, requires Cl = 6.9 per cent., whereas Elbs (*loc. cit.*) finds 6.6 per cent.

*Platinichloride*,  $[\text{C}_{21}\text{H}_{18}(\text{C}_7\text{H}_7)_2\text{ON}_2]_2\text{H}_2\text{PtCl}_6$ .—Orange-coloured, microscopic needles, melting at 195.5° (206°, Elbs).

0.5133 gave 0.0714 Pt. Pt = 13.91.

0.6094 „ 0.0845 Pt. Pt = 13.90.

$[\text{C}_{21}\text{H}_{18}(\text{C}_7\text{H}_7)_2\text{ON}_2]_2\text{H}_2\text{PtCl}_6$  requires Pt = 13.95 per cent.

*Nitrate*.—Not analysed. Prepared by adding nitric acid to a glacial acetic acid solution of the base, and then diluting. Rosettes of thick prisms from alcohol on addition of ether. Melts at 174°, evolving gas and turning yellow. The products of the decomposition by heat are described in the next section.

*Action of Heat on the Salts of the Base*,  $\text{C}_{21}\text{H}_{18}(\text{C}_7\text{H}_7)_2\text{ON}_2$ .—The foregoing hydrochloride of the base was heated at 220° for a few minutes. Vapours were evolved, having a slight odour of benzylic chloride. The residue, purified by solution in chloroform and precipitation with ether, was dissolved in alcohol and treated with aqueous ammonia, to precipitate unaltered base. There was hardly any precipitate, and the non-precipitated portion proved to be dibenzylamaronium chloride; when isolated, it melted at 38—45°. It was further identified by conversion into the dichromate,  $[\text{C}_{21}\text{H}_{17}(\text{C}_7\text{H}_7)_2\text{N}_2\text{Cl}]_2\text{H}_2\text{Cr}_2\text{O}_7$ , which showed the correct melting point of 173°. The mechanism of the change by which "dibenzylamarine" hydrochloride is converted, with elimination of water, into dibenzylamaronium chloride, is discussed in the introduction to this paper.

The hydrochloride of "dibenzylamarine" was heated in the same way at

185°; it turned brown and gave off a vapour smelling like nitrobenzene. The residue, dissolved in alcohol, deposited a quantity of the nitroso-derivative of "dibenzylamarine" which melted at 167° (see following section), and the mother liquor, on addition of ether, gave leaflets, which, after frequent recrystallisation from benzene, melted at 157°, and were identical with the synthetic dibenzylamaronium nitrate already described.

*Action of Nitrous Acid on the Compound*  $C_{21}H_{18}(C_7H_7)_2ON_2$ .—"Dibenzylamarine" was dissolved in glacial acetic acid, the solution was slightly diluted with water, and an equal weight of sodium nitrite was gradually added. A white, crystalline compound separated, and was purified by recrystallisation from alcohol, from which it was deposited in rectangular laminæ melting constantly at 168°. It is readily soluble in chloroform, and on adding ether to the solution, separates in long, flat needles. It is not altered by ammonia, or by alcoholic potassium hydroxide even at 150°. It gives Liebermann's reaction for nitroso-compounds.

0.1180 gave 0.3461  $CO_2$  and 0.0636  $H_2O$ .  $C=79.99$ ;  $H=5.99$ .

0.1117 „ 0.3270  $CO_2$  „ 0.0585  $H_2O$ .  $C=79.84$ ;  $H=5.82$ .

0.2880 „ 20.75 c.c. moist nitrogen at 14° and 735 mm.  $N=8.19$ .

$C_{35}H_{31}O_2N_3$  requires  $C=80.00$ ;  $H=5.90$ ;  $N=8.00$  per cent.

The compound is the *nitrosamine* of *benzoyl-s-dibenzyl-i-diphenylethylenediamine*, and has the constitution

$$\begin{array}{c} C_6H_5 \cdot CH \cdot N(C_7H_7) \cdot CO \cdot C_6H_5 \\ C_6H_5 \cdot CH \cdot N(C_7H_7) \cdot NO \end{array}$$

It differs, both in its physical properties and in its resistance to the action of potassium hydroxide, from the isomeric dibenzylamaronium nitrite.

When the nitrosamine is heated above its melting point, it evolves gas, and yields, as chief solid product, lophine, which was identified both by its properties and by analysis.

In the preparation of the nitrosamine, especially when excess of sodium nitrite was employed and the mixture was heated, the alcoholic mother liquors gave, on dilution, needles of lophine, together with an oily substance. By extracting the latter with alcohol, a very soluble substance was removed and some nitrosamine was left. The soluble substance, which remained on evaporation of the alcohol, was crystallised, first from benzene, with the addition of light petroleum, and afterwards from alcohol, with the addition of ether. It was thus ob-

\* In the first preparation of this substance, we obtained it also in short, slender needles melting at 166°, and in our preliminary note (Proc., 1899, 15, 227), described it as dimorphous. We have been unable to obtain this form in subsequent experiments.

tained in very lustrous, thin, rectangular leaflets melting at  $157-158^{\circ}$ . The substance is *dibenzylamaronium nitrate*,  $C_{21}H_{17}(C_7H_7)_2N_2 \cdot NO_3$ .

0.1718 gave 0.4878  $CO_2$  and 0.0936  $H_2O$ .  $C = 77.44$ ;  $H = 6.05$ .

0.2857 „ 18.95 c.c. moist nitrogen at  $11.5^{\circ}$  and 744 mm.  $N = 7.72$ .  $C_{21}H_{17}(C_7H_7)_2N_2 \cdot NO_3$  requires  $C = 77.63$ ;  $H = 5.73$ ;  $N = 7.76$  per cent.

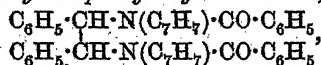
It was indistinguishable from the synthetic nitrate prepared from dibenzylamaronium chloride and silver nitrate, and, like this compound, is stable towards ammonia in the cold, but is decomposed by potassium hydroxide with formation of “dibenzylamarine.”

*Action of Benzoic Chloride on the Compound*  $C_{21}H_{18}(C_7H_7)_2ON_2$ .—“Dibenzylamarine” was boiled with benzoic chloride for a few minutes. Addition of ether precipitated a crystalline substance which was almost insoluble in alcohol, but could be recrystallised from a large bulk of benzene, adding a little light petroleum to start the crystallisation. It formed microscopic, six-sided or lozenge-shaped plates, melting at  $268^{\circ}$ . It may also be readily recrystallised by dissolving it in chloroform and adding ether. A nitrogen determination showed that a benzoyl group had been introduced into the molecule of “dibenzylamarine.”

0.2230 gave 9.00 c.c. moist nitrogen at  $12^{\circ}$  and 756 mm.  $N = 4.77$ .

$C_{42}H_{36}O_2N_2$  requires  $N = 4.67$  per cent.

It is *s-dibenzoyldibenzyl-i-diphenylethylenediamine*,



and is quite distinct from the isomeric dibenzylamaronium benzoate. The latter is an uncrystallisable gum, which is converted by warming with alcoholic potassium hydroxide into “dibenzylamarine,” whereas the present crystalline compound is unaffected by this reagent even at  $150^{\circ}$ .

*Reduction of the Compound*  $C_{21}H_{18}(C_7H_7)_2ON_2$  *with Hydriodic Acid*.—A mixture of 20 grams of “dibenzylamarine,” 10 grams of amorphous phosphorus, and 200 grams of hydriodic acid of sp. gr. 1.7, was boiled for 5 hours, using a reflux tube. On cooling, a considerable quantity of crystals separated. The whole was filtered, and the dried cake of substance was disintegrated by extraction with excess of ether. The undissolved residue (a) consisted of the hydriodide of a compound,  $C_{28}H_{26}ON_2$ , mixed with excess of phosphorus. The ethereal extract (b) contained benzylic iodide, dibenzyl, and benzoic acid. The original hydriodic acid filtrate was diluted and neutralised with sodium hydroxide; it gave a flocculent precipitate (c) consisting of the compound  $C_{28}H_{26}ON_2$ , with a further compound,  $C_{21}H_{22}N_2$ . The rate from this precipitate was steam distilled, and the distillate (d) contained benzylamine and ammonia.



The following methods were employed in the isolation and examination of these various substances.

The undissolved residue (a) was extracted several times with boiling alcohol; the solution on cooling gave prismatic needles of a hydriodide melting at  $217^{\circ}$ . These were redissolved by heating, and ammonia was added, causing an immediate bulky precipitate of a sparingly soluble base. It was practically pure, and the yield was 8 grams. For analysis, a portion of it was recrystallised from a large bulk of boiling alcohol; it formed minute needles melting at  $218.5^{\circ}$ . It is fairly soluble in chloroform, and may be recrystallised from this solvent. It is very stable, and, when heated in a vacuum at  $280^{\circ}$ , distilled in part unchanged. Analysis gave figures agreeing with the formula  $C_{23}H_{26}ON_2$ .

0.1385 gave 0.4191  $CO_2$  and 0.0814  $H_2O$ .  $C = 82.53$ ;  $H = 6.53$ .

0.1260 „ 0.3806  $CO_2$  „ 0.0737  $H_2O$ .  $C = 82.38$ ;  $H = 6.50$ .

0.2492 „ 14.95 c.c. moist nitrogen at  $15^{\circ}$  and 750.5 mm.  $N = 6.94$ .

$C_{23}H_{26}ON_2$  requires  $C = 82.75$ ;  $H = 6.40$ ;  $N = 6.90$  per cent.

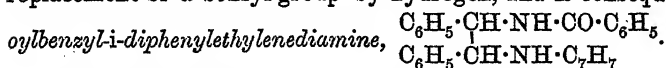
Iodine was determined in the recrystallised *hydriodide* (m. p.  $217^{\circ}$ ):

1.0172 gave 0.4428 AgI.  $I = 23.52$ .

$C_{23}H_{26}ON_2 \cdot HI$  requires  $I = 23.78$  per cent.

The *hydrochloride* (not analysed) is a microcrystalline powder melting at  $256-258^{\circ}$ .

The base,  $C_{23}H_{26}ON_2$ , is formed from "dibenzylamarine" by the replacement of a benzyl group by hydrogen, and is consequently *benzoylbenzyl-i-diphenylethylenediamine*,



The presence of an imino-group in this compound is shown by the formation of a nitrosamine, which was obtained as follows. The compound,  $C_{23}H_{26}ON_2$ , was dissolved in excess of glacial acetic acid, and a solution of nitrous acid in acetic acid (prepared by adding sodium nitrite to glacial acetic acid and then diluting slightly to dissolve the sodium diacetate) was mixed with it. An insoluble nitrosamine was precipitated. It was filtered off, washed with acetic acid, first glacial, then dilute, and finally with alcohol. It melted at  $246^{\circ}$ .

0.1915 gave 15.65 c.c. moist nitrogen at  $15^{\circ}$  and 772 mm.  $N = 9.72$ .

$C_{23}H_{25}O_2N_3$  requires  $N = 9.65$  per cent.

The compound is  $\begin{array}{c} C_6H_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot C_6H_5 \\ | \\ C_6H_5 \cdot \text{CH} \cdot \text{N} \cdot (C_7H_7) \cdot \text{NO} \end{array}$

An attempt which we made to convert benzoylbenzyl-i-diphenylethylenediamine hydrochloride by the action of heat into benzyl-

amarine hydrochloride and water—a reaction which would have corresponded with the transformation of “dibenzylamarine” hydrochloride into dibenzylamaronium chloride—proved unsuccessful.

The ethereal extract (b), on distilling off the ether, left an oil with the irritating smell of the benzylic halides. On heating a small quantity in a test-tube, it decomposed giving off iodine, and doubtless contained *benzylic iodide*. The remainder of the oil, after heating on the water-bath until the benzylic iodide was volatilised, solidified on cooling. By means of sodium hydroxide, it was separated into *benzoic acid*—identified by its physical properties—and a hydrocarbon; the latter proved to be *dibenzyl*, and after recrystallisation, first from light petroleum and then from methylic alcohol, melted at  $52.5^{\circ}$  (m. p. of dibenzyl,  $52^{\circ}$ ), whilst its cold supersaturated solution crystallised instantaneously on introducing a crystal of a known specimen of dibenzyl.

0.1123 gave 0.3800  $\text{CO}_2$  and 0.0809  $\text{H}_2\text{O}$ . C = 92.29; H = 8.00.

$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$  requires C = 92.30; H = 7.70 per cent.

The flocculent precipitate (c) was extracted with alcohol; this removed a readily soluble base, leaving a residue of impure benzoyl-benzyl-*i*-diphenylethylenediamine. The alcoholic solution, on concentration and dilution, gave long needles of the readily soluble base. It was found that it could be best purified by expelling the alcohol, dissolving the residue in dilute hydrochloric acid, filtering from resinous matter, reprecipitating with sodium hydroxide, and recrystallising twice from methylic alcohol by dilution with water. By drying the substance thus obtained and washing with a few drops of ether, it was obtained in a colourless condition. It formed long needles melting at  $90^{\circ}$ . Analysis gave figures agreeing with the formula  $\text{C}_{21}\text{H}_{22}\text{N}_2$ .

0.1380 gave 0.4209  $\text{CO}_2$  and 0.091  $6\text{H}_2\text{O}$ . C = 83.18; H = 7.37.

0.2233 „ 17.15 c.c. moist nitrogen at  $6.5^{\circ}$  and 752 mm. N = 9.24.

$\text{C}_{21}\text{H}_{22}\text{N}_2$  requires C = 83.44; H = 7.28; N = 9.27 per cent.

The substance contains four atoms of hydrogen more than amarine, and is therefore an open-chain compound: namely, *benzyl-i-diphenyl-*

*ethylenediamine*,  

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH}_2 \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{C}_7\text{H}_7 \end{array}$$

According to the constitutions which we have assigned to this compound and to the compound  $\text{C}_{28}\text{H}_{26}\text{ON}_2$  (m. p.  $218.5^{\circ}$ ), the latter is a benzoyl derivative of the former. Experiment confirmed this view. A small quantity of the compound  $\text{C}_{21}\text{H}_{22}\text{N}_2$  was heated with excess of benzoic chloride for an hour at  $100^{\circ}$ . At first it dissolved, but speedily the hydrochloride of the base  $\text{C}_{28}\text{H}_{26}\text{ON}_2$  separated; this was filtered off, washed with cold alcohol, dissolved in boiling alcohol, and precipi-

tated with ammonia. The sparingly soluble base formed minute, white needles, identical with those of the compound  $C_{28}H_{26}ON_2$  and melting at  $218^\circ$ . This identity was confirmed by a nitrogen determination.

0.1379 gave 8.30 c.c. moist nitrogen at  $21.5^\circ$  and 767 mm.  $N = 6.90$ .

$C_{28}H_{26}ON_2$  requires  $N = 6.90$  per cent.

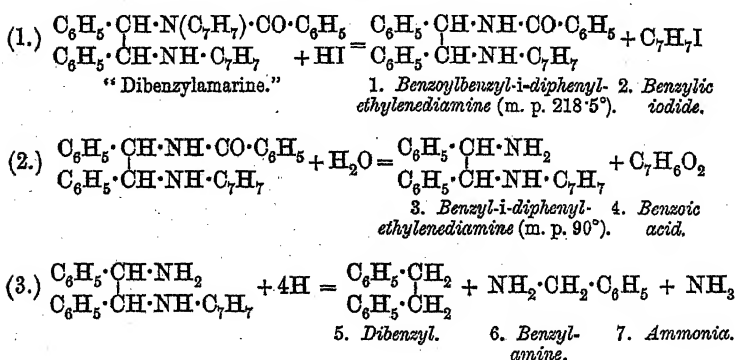
The compound  $C_{28}H_{26}ON_2$  is, therefore, as already stated, *benzoyl-benzyl-i-diphenylethylenediamine*.

The opalescent steam distillate (*d*) which smelt of ammonia, was acidified with hydrochloric acid and evaporated to dryness. The product was a mixture of lustrous laminae of benzylamine hydrochloride with ammonium chloride. (On adding sodium hydroxide to a portion, free benzylamine separated as an oil.) The mixed chlorides were extracted with boiling absolute alcohol, which dissolved the benzylamine hydrochloride; on treating the residue with sodium hydroxide, only ammonia was liberated. Alcoholic platonic chloride was added to the alcoholic solution, and, after digestion on the water-bath, the liquid was filtered hot to remove a little ammonium platinichloride. On cooling, *benzylamine* platinichloride separated in lustrous, yellow scales melting at  $229^\circ$ , and identical with a specimen prepared from benzylamine. It was again crystallised from alcohol, to remove the last trace of ammonium platinichloride. Only a small quantity was available for analysis.

0.0872 gave 0.0272 Pt.  $Pt = 31.19$ .

$(C_6H_5 \cdot CH_2 \cdot NH_2)_2, H_2PtCl_6$  requires  $Pt = 31.25$  per cent.

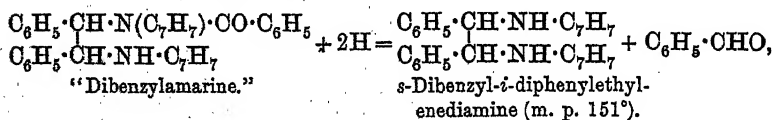
If we regard "*dibenzylamarine*" as benzoyl-*s*-dibenzyl-*i*-diphenylethylenediamine, the formation of the seven compounds obtained in the hydriodic acid reduction may be expressed by the following equations:



*Reduction of the Compound  $C_{21}H_{18}(C_7H_7)_2ON_2$  with Sodium in Boiling Amylic Alcohol.*—5 grams of "*dibenzylamarine*" were dis-

solved in 100 grams of anhydrous amyllic alcohol, and to the boiling solution, 5 grams of sodium were gradually added: the liquid became yellow. The product was treated several times with water to destroy sodium amyloxyde, rejecting the aqueous portions, evaporating the turbid amyl-alcoholic solution to dryness on a water-bath, and boiling the residue with water to expel the last traces of amyllic alcohol. This residue, after treatment with ether, consisted of fairly pure *s*-dibenzyl-*i*-diphenylethylenediamine, which, after recrystallisation from alcohol, formed colourless needles, or thin, four-sided prisms melting at 151° and giving a hydrochloride melting at 242°. On comparison with a specimen of Grossmann's *s*-dibenzyl-*i*-diphenylethylenediamine, prepared by the reduction of dibenzylidene-*i*-diphenylethylenediamine (m. p. 164°) with sodium in amyllic alcohol (*Ber.*, 1889, 22, 2301), the two were found to be identical. Grossmann gives the melting point as 153°; but we found that complete purification, by removing traces of the dibenzylidene derivative, lowers the melting point to 150·5°.

We satisfied ourselves that "dibenzylamarine" is not altered by boiling it with a solution of sodium amyloxyde in amyllic alcohol. The removal of the benzoyl group in the foregoing reaction is, therefore, due, not to hydrolysis, but to the action of the nascent hydrogen:



the benzaldehyde being of course further acted on.

We did not analyse the compound thus obtained, as we had already made a full analysis of the same substance prepared from "dibenzylamarine" by fusion with potassium hydroxide (see following section).

*Action of Potassium Hydroxide on the Compound*  $\text{C}_{21}\text{H}_{18}(\text{C}_7\text{H}_7)_2\text{ON}_2$ .—The experiment of heating "dibenzylamarine" with a strong solution of potassium hydroxide in methylic alcohol at 160° gave no result: the substance was recovered quite unaltered. Fusion with potassium hydroxide was therefore resorted to.

10 grams of "dibenzylamarine" were stirred into 30 grams of fused potassium hydroxide (to which a little water had been previously added) at a temperature of 220°, after which the temperature was slowly raised to 240° and kept at 240—250° for five minutes. The mixture at first frothed, giving off a vapour which smelt like benzylic cyanide; afterwards it became more solid. The product was treated with water; the undissolved organic portion was taken up with ether; and the ethereal solution was dried by solid potassium hydroxide and saturated with gaseous hydrogen chloride. This produced a bulky,

sticky precipitate of hydrochlorides, from which the mother liquor was decanted and evaporated, leaving a yellow gum (which solidified on standing) consisting of non-basic products.

The hydrochlorides, dissolved in alcohol, gave, on concentration, needle-shaped crystals, which, when re-dissolved in alcohol and precipitated with ammonia, yielded a base sparingly soluble in cold alcohol. It was found to be contaminated with tetraphenylazine; this was readily removed by its very sparing solubility in alcohol. Thus purified, the base formed colourless needles melting at  $150^{\circ}$ , and was identical with Grossmann's *dibenzyl-i-diphenylethylenediamine* already referred to.

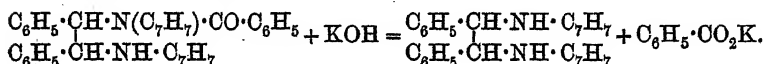
0.1279 gave 0.4007  $\text{CO}_2$  and 0.0851  $\text{H}_2\text{O}$ .  $\text{C}=85.44$ ;  $\text{H}=7.39$ .

0.2435 „ 14.90 c.c. moist nitrogen at  $16^{\circ}$  and 762 mm.  $\text{N}=7.15$ .

$\text{C}_{28}\text{H}_{28}\text{N}_2$  requires  $\text{C}=85.71$ .  $\text{H}=7.14$ ;  $\text{N}=7.14$  per cent.

The hydrochloride was also prepared from the pure base and compared with that of Grossmann's compound. They were identical; both melted at  $242^{\circ}$ .

In the present case the base is formed according to the equation



The alcoholic mother liquor, from the crude hydrochloride, was treated with oxalic acid and ether. From the mixture of oxalates which separated, more of Grossmann's base was obtained, together with some unchanged "dibenzylamarine." The filtrate from the oxalates contained benzyllophine, which showed the characteristic dimorphism—needles and square plates—and melted at  $164.5^{\circ}$ . (m. p. of benzyllophine,  $165^{\circ}$ ). The crystallisation of a supersaturated solution was instantaneously started by the addition of a crystal of benzyllophine. The yield of benzyllophine was small, and probably the potassium hydroxide had nothing to do with its production, as we obtained the same substance in greater quantity by heating "dibenzylamarine" alone (see later on).

The yellow, non-basic gum was dissolved in alcohol. Colourless prismatic crystals separated, and after recrystallisation from the same solvent, melted constantly at  $127-128^{\circ}$ . The results of analysis agreed best with the formula  $\text{C}_{25}\text{H}_{24}\text{ON}_2$ .

0.1428 gave 0.4354  $\text{CO}_2$  and 0.0832  $\text{H}_2\text{O}$ .  $\text{C}=83.15$ ;  $\text{H}=6.47$ .

0.1338 „ 0.4086  $\text{CO}_2$  „ 0.0761  $\text{H}_2\text{O}$ .  $\text{C}=83.29$ ;  $\text{H}=6.32$ .

0.1863 „ 11.10 c.c. moist nitrogen at  $11.5^{\circ}$  and 761.5 mm.  $\text{N}=7.09$ .

$\text{C}_{25}\text{H}_{24}\text{ON}_2$  requires  $\text{C}=83.17$ .  $\text{H}=5.94$ ;  $\text{N}=6.93$  per cent.

We give this formula with reserve. Until some more productive method of preparing the compound is discovered, it will be impossible to study its reactions.

*Oxidation of the Compound  $C_{21}H_{18}(C_7H_7)_2ON_2$  with Chromium Trioxide in presence of Hydrochloric Acid.*—Claus (Ber., 1882, 15, 2330) mentions that "dibenzylamarine" is not altered by boiling with chromium trioxide in glacial acetic acid solution. This is correct; but we found that, just as in the reaction with dibenzylamaronium chloride, oxidation takes place if hydrochloric acid is added to the mixture, the action being doubtless due to liberated chlorine.

10 grams of "dibenzylamarine" were dissolved in a little glacial acetic acid, and a solution of 10 grams of chromium trioxide in the same solvent was added. The resulting cake of "dibenzylamarine" dichromate was pressed to remove the mother liquor, and boiled with fresh glacial acetic acid, gradually adding from 15 to 20 c.c. of concentrated hydrochloric acid, and boiling until the chromium trioxide was reduced. On diluting with water, an oil separated, more of it being obtained by extracting the solution with chloroform. The oil was dissolved in alcohol, and ammonia added; this occasioned a precipitate of minute needles, which by recrystallisation from boiling alcohol, in which they are only sparingly soluble, were obtained pure, melting constantly at  $218^\circ$ . The substance was identical with benzoylbenzyl-

*i*-diphenylethylenediamine,  $C_6H_5 \cdot \underset{\text{C}_6H_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6H_5}{\text{CH} \cdot \text{NH}} \cdot C_6H_5$ , already obtained

by the reduction of "dibenzylamarine" with hydriodic acid, having been formed in the present case by the removal of a benzyl group from the "dibenzylamarine" in the process of oxidation. The yield was very poor compared with that obtained by the reduction process.

0.1545 gave 0.4687  $CO_2$  and 0.0897  $H_2O$ . C=82.73; H=6.45.

0.1544 " 0.4675  $CO_2$  " 0.0897  $H_2O$ . C=82.58; H=6.46.

0.2700 " 15.60 c.c. moist nitrogen at  $13^\circ$  and 769 mm. N=6.90.

0.2317 " 13.38 c.c. " "  $13.5^\circ$  " 770 mm. N=6.89.

$C_{25}H_{26}ON_2$  requires C=82.75; H=6.40; N=6.90 per cent.

A simultaneous determination of the melting point of the hydriodide of this base and of that obtained by the reduction process gave  $217^\circ$  in both cases, the substances turning brown.

The mother liquor from the foregoing base yielded a compound melting at  $127^\circ$ . It contained chlorine which could be removed by alcoholic potassium hydroxide; but the quantity of substance was insufficient for further investigation.

The only other product of oxidation observed was benzoic acid.

*Action of Heat on the Compound  $C_{21}H_{18}(C_7H_7)_2ON_2$ .*—10 grams of "dibenzylamarine" were introduced into an Anschütz flask (with

receiver fused to the tubulure), which was then exhausted and heated by means of a graphite bath. Decomposition proceeded slowly, requiring a high temperature. There was only a small quantity of yellow, viscous distillate, smelling of dibenzyl; and the operation was stopped when a sublimation of crystals commenced. The substance in the flask was extracted with boiling alcohol; the residue, which formed by far the greater part, consisted of *lophine*, and, after purification by sublimation, melted at  $274^{\circ}$ . The alcoholic extract was evaporated to dryness, and the residue extracted with boiling benzene; *lophine* remained undissolved, and the benzene extract, on concentration, gave square plates of *benzyllophine*. On recrystallisation from boiling alcohol it was obtained in needles and square plates—the dimorphous forms of benzyllophine—both melting at  $164^{\circ}$ . A supersaturated solution instantly crystallised on introducing a crystal of benzyllophine.

*Synthesis of the Compound*  $C_{21}H_{18}(C_7H_7)_2ON_2$  ("*Dibenzylamarine*") from *s*-Dibenzyl-*i*-diphenylethylenediamine.—Grossmann (*Ber.*, 1899, 22, 2301) obtained *s*-dibenzyl-*i*-diphenylethylenediamine by reducing dibenzylidene-*i*-diphenylethylenediamine,  $C_6H_5 \cdot CH \cdot N : CH \cdot C_6H_5$ , with  $C_6H_5 \cdot CH \cdot N : CH \cdot C_6H_5$ ,

sodium in boiling alcohol. Although, from this mode of formation, the compound in all probability had the symmetrical constitution, we nevertheless thought it desirable to find independent proof of this, as a migration, depending upon the intermediate formation of a cyclic compound (compare *Trans.*, 1895, 67, 33–34), was not absolutely excluded. We therefore studied the action of nitrous acid on Grossmann's compound.

Dibenzyl-*i*-diphenylethylenediamine, prepared by Grossmann's method was dissolved in glacial acetic acid, and a solution of nitrous acid in acetic acid (prepared by dissolving sodium nitrite in slightly diluted acetic acid) was added in the cold. A precipitate of slender needles, almost insoluble in the ordinary solvents, was formed, and after purifying it by boiling with alcohol, melted at  $233^{\circ}$ . It gives Liebermann's nitroso-reaction very strongly. A nitrogen determination showed that two nitroso-groups had been introduced, thus proving the symmetrical constitution of Grossmann's dibenzyl-*i*-diphenylethylenediamine.

0.1097 gave 11.50 c.c. moist nitrogen at  $15^{\circ}$  and 772 mm.  $N = 12.47$ .  
 $C_{28}H_{26}(NO)_2N_2$  requires  $N = 12.44$  per cent.

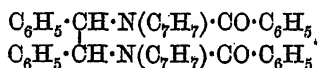
It has the constitution  $C_6H_5 \cdot CH \cdot N(C_7H_7) \cdot NO$   
 $C_6H_5 \cdot CH \cdot N(C_7H_7) \cdot NO$

The view which we had formed concerning the constitution of "dibenzylamarine" pointed to the possibility of preparing the latter compound by the introduction of a benzoyl group into *s*-dibenzyl-*i*-

diphenylethylenediamine, or of preparing benzoyl-"dibenzylamarine" by the introduction of two benzoyl groups. Experiment confirmed both these suppositions; but the conditions necessary for success are more easily realised in the latter than in the former case.

*s*-Dibenzyl-*i*-diphenylethylenediamine was mixed with excess of benzoic chloride and gently warmed, when it dissolved; but on heating for 5 minutes at 100°, the whole solidified, yielding a mixture of the dibenzoyl derivative with hydrochloride of the unaltered base. The two substances were readily separated by the almost total insolubility of the former compound in alcohol.

By benzoylating dibenzyl-*i*-diphenylethylenediamine by the Schotten-Baumann method, the whole was converted into dibenzoyl compound. The product was disintegrated by boiling with alcohol, and recrystallised from benzene. It agreed in melting point (268°) and crystalline form with the compound already obtained by the action of benzoic chloride on "dibenzylamarine"—benzoyl-"dibenzylamarine"—which is therefore *s*-dibenzoyldibenzyl-*i*-diphenylethylenediamine,



In order to obtain the monobenzoyl derivative, 2 grams of *s*-dibenzyl-*i*-diphenylethylenediamine were dissolved in excess of benzene, 1 gram of benzoic chloride was added and the mixture was digested on the water-bath until a precipitate of hydrochloride was produced; this was separated, and the benzene solution, after adding alcohol, was evaporated to dryness. The gummy residue was warmed with alcoholic potassium hydroxide, which dissolved it; on diluting slightly with water, a trace of the foregoing dibenzoyl derivative separated and was removed by filtration; and on further dilution a substance was deposited in rosettes of needles, which, after recrystallisation from benzene with the addition of light petroleum, melted constantly at 139.5°, and were indistinguishable from those of Claus and Elbs's "dibenzylamarine" (m. p. 139°). The platinichloride prepared from it melted at 195.5°, which agrees with the melting point found by us for the salt from Claus and Elbs's base, and under the microscope the two salts were also indistinguishable from one another. Platinum was determined; but the amount of substance at our disposal was too small for a perfectly trustworthy analysis.

0.1194 gave 0.0175 Pt.  $\text{Pt} = 14.64$ .

•  $[\text{C}_{21}\text{H}_{18}(\text{C}_6\text{H}_5)_2\text{ON}_2]_2 \cdot \text{H}_2\text{PtCl}_6$  requires  $\text{Pt} = 13.95$  per cent.

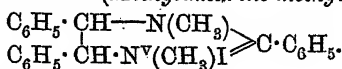
This difference is due to the smallness of the quantity of substance taken, and would be accounted for by an error of 0.8 mg. in the weight of platinum.



Claus and Elbs's so-called dibenzylamarine is therefore benzoyl-  
*s-dibenzyl-i-diphenylethylenediamine*, 
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N}(\text{C}_7\text{H}_7) \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{C}_7\text{H}_7 \end{array}$$

### B. Dimethyl Derivatives.

*Dimethylamaronium Iodide (Methylamarine-methylic Iodide,*



—The method described by Elbs (*Inaugural-Dissertation*, pp. 12—13) was followed in the preparation of this compound. 100 grams of amarine and 55 grams of methylic iodide were dissolved in ether and allowed to stand for from a week to a fortnight. The liquid was decanted and the crust of crystals—a mixture of the quaternary iodide with amarine hydriodide—was treated with chloroform, which dissolved only the former substance; this was precipitated from the concentrated chloroform solution by ether and recrystallised from alcohol, from which it was deposited in lustrous octahedra, melting at 247°. The yield was about 40 grams. An iodine determination gave  $\text{I} = 27.82$ .  $\text{C}_{23}\text{H}_{23}\text{N}_2\text{I}$  requires  $\text{I} = 27.98$  per cent. Ammonia is without action on it,

The foregoing agrees with Claus and Elbs's description.

*Claus and Elbs's "Dimethylamarine."*—This was prepared by warming dimethylamaronium iodide with alcoholic potassium hydroxide, as prescribed by Claus and Elbs (*loc. cit.*). It forms large, powerfully refractive prismatic crystals, melting at 145° (146°, Claus and Elbs). We can confirm the observations of these authors regarding the preparation and properties of the compound; but, as in the case of "dibenzylamarine," our analyses lead to a formula containing the elements of a mol. of water more than the formula adopted by them. The substance does not lose weight at 105°.

0.1660 gave 0.4865  $\text{CO}_2$  and 0.1043  $\text{H}_2\text{O}$ .  $\text{C} = 79.93$ ;  $\text{H} = 6.98$ .  
 0.1432 „ 0.4201  $\text{CO}_2$  „ 0.0869  $\text{H}_2\text{O}$ .  $\text{C} = 80.01$ ;  $\text{H} = 6.74$ .  
 0.2016 „ 0.5938  $\text{CO}_2$  „ 0.1314  $\text{H}_2\text{O}$ .  $\text{C} = 80.33$ ;  $\text{H} = 7.24$ . }  
 0.1632 „ 0.4782  $\text{CO}_2$  „ 0.1032  $\text{H}_2\text{O}$ .  $\text{C} = 79.92$ ;  $\text{H} = 7.03$ . }  
 0.2334 „ 16.70 c.c. moist nitrogen at 14° and 733 mm.  $\text{N} = 8.12$ .  
 $\text{C}_{23}\text{H}_{24}\text{ON}_2$  requires  $\text{C} = 80.23$ ;  $\text{H} = 6.97$ ;  $\text{N} = 8.14$  per cent.

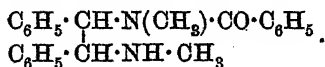
The formula of a dimethylamarine,  $\text{C}_{21}\text{H}_{16}(\text{CH}_3)_2\text{N}_2$ , on the other hand, would require  $\text{C} = 84.66$ ;  $\text{H} = 6.76$ ;  $\text{N} = 8.59$  per cent.

No analysis of this compound is given in Claus and Elbs's paper. Moreover, Elbs (*loc. cit.*) gives a reason for not analysing it: namely,

\* Combustions III and IV were made by Mr. A. N. Meldrum.

that analysis would not distinguish between methylamarine and dimethylamarine. Analysis, however, shows that it is neither.

Following the analogy of the supposed dibenzylamarine, the compound is doubtless *benzoyl-s-dimethyl-i-diphenylethylenediamine*,



The *platinichloride* is a yellow, microcrystalline powder, melting, somewhat indefinitely, at 183° (185°, Elbs). It did not lose weight at 95°.

0.2463 gave 0.0436 Pt. Pt = 17.70.

$[\text{C}_{21}\text{H}_{18}(\text{CH}_3)_2\text{ON}_2]_2\text{H}_2\text{PtCl}_6$  requires Pt = 17.76 per cent.

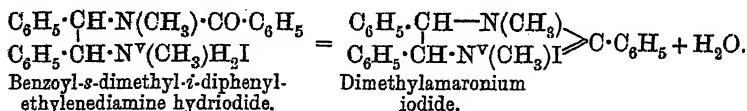
Claus and Elbs's formula would require, on the other hand, Pt = 18.5 per cent.

The *hydriodide*, which was prepared by Claus and Elbs, was obtained by dissolving the base in aqueous hydriodic acid, decolorising with a very little sulphurous acid. It formed rosettes of prismatic crystals melting, frothing up, and resolidifying at 200°. It is, as stated by Claus and Elbs, quite distinct from dimethylamaronium iodide, and is instantaneously decomposed by ammonia, even in the cold.

*Action of Heat on the Hydriodide of the Base*,  $\text{C}_{21}\text{H}_{18}(\text{CH}_3)_2\text{ON}_2$ .—The dry hydriodide was heated at 210–220° in a paraffin bath. It melted, frothing up in the process, and afterwards resolidified at the same temperature. On dissolving the product in alcohol and adding ether, octahedral crystals of *dimethylamaronium iodide* were obtained. They melted at 246°, and were not decomposed by ammonia.

This melting, frothing up, and resolidifying was observed by Elbs (*loc. cit.*, p. 17), but he neglected to investigate the cause of the phenomenon.

The transformation of the hydriodide into the quaternary iodide takes place according to the equation,



This transformation takes place slowly, even on boiling the hydriodide with aqueous hydriodic acid.

### C. Diethyl Derivatives.

*Diethylamaronium Iodide*,  $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N}(\text{C}_2\text{H}_5) \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N}^+(\text{C}_2\text{H}_5)_2\text{I} \end{array} \gg \text{C} \cdot \text{C}_6\text{H}_5$ .—This substance was prepared by Borodin (*Annalen*, 1859, 110, 82), who called it "diethylamarine hydriodide."

We first tried to prepare it by the method which we have described in the case of dimethylamaronium iodide; but the action took place so slowly in the cold that we found it necessary to employ heat.

50 grams of amarine and 30 grams of ethylic iodide were boiled in alcoholic solution for 6 hours. As the quaternary iodide and the amarine hydriodide which were formed had practically the same solubility in all solvents which we tried, and as Borodin's process of mechanically separating the two kinds of crystals is tedious and unsatisfactory, we distilled off most of the alcohol, and, to the cooled solution, added ammonia (which decomposed the hydriodide, leaving the quaternary salt unaltered), and then water. The precipitated oil consisted of a mixture of the quaternary iodide with amarine. A further quantity of oil was obtained by extracting the aqueous liquid with chloroform and evaporating the latter. The oily substance was dissolved in alcohol, and ether was added; on standing, lustrous, oblique crystals of diethylamaronium iodide were deposited, the amarine remaining in solution. The substance melted sharply and constantly at  $203^{\circ}$  ( $200$ — $210^{\circ}$ , Borodin). An iodine determination gave  $I = 26.12$ .  $C_{25}H_{27}N_2I$  requires  $I = 26.35$  per cent.

The constitution, based on the analogy of the dibenzyl compound, has just been given.

*Borodin's "Diethylamarine."*—This was obtained by warming the quaternary iodide with alcoholic potassium hydroxide. Recrystallised from slightly diluted alcohol, it formed lustrous, flat needles melting at  $125^{\circ}$  ( $110$ — $115^{\circ}$ , Borodin).

Analysis showed that it is not a diethylamarine, as supposed by Borodin, but, like the analogous dimethyl and dibenzyl compounds, contains the elements of a mol. of water more than the formula of a dialkylamarine would require.

0.1532 gave 0.4539  $CO_2$  and 0.1065  $H_2O$ .  $C = 80.80$ ;  $H = 7.72$ .

0.1566 „ 0.4614  $CO_2$  „ 0.1055  $H_2O$ .  $C = 80.35$ ;  $H = 7.49$ .

0.1571 „ 0.4642  $CO_2$  „ 0.1082  $H_2O$ .  $C = 80.58$ ;  $H = 7.65$ .

0.1442 „ 0.4252  $CO_2$  „ 0.1006  $H_2O$ .  $C = 80.42$ ;  $H = 7.75$ .\*

0.2750 „ 18.45 c.c. moist nitrogen at  $18^{\circ}$  and 753 mm.  $N = 7.68$ .

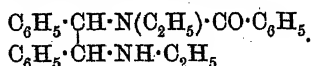
$C_{25}H_{28}ON_2$  requires  $C = 80.65$ ;  $H = 7.53$ ;  $N = 7.53$ .

The formula of a diethylamarine,  $C_{21}H_{16}(C_2H_5)_2N_2$ , on the other hand, would require  $C = 84.74$ ;  $H = 7.34$ ;  $N = 7.91$  per cent. Borodin found  $C = 84.69$ ,  $84.84$ ;  $H = 7.34$ ,  $7.63$ . It seems just possible that he may have analysed unchanged amarine, although the hydrogen is somewhat high for this.

Our analyses, however, show that Borodin's formula is inadmissible.

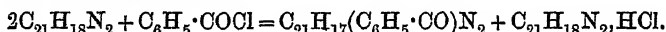
\* Combustion IV was made by Mr. A. N. Meldrum.

On the analogy of the dibenzyl derivative, we regard the compound as *benzoyl-s-diethyl-i-diphenylethylenediamine*,



## II. BENZOYLAMARINE AND THE SUPPOSED DIACYLAMARINES.

*Benzoylamarine*,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N} \begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{C} \cdot \text{C}_6\text{H}_5 \end{array} \text{C}_6\text{H}_5$ .—We prepared this compound at first by the method described by Claus and Scherbel (*Ber.*, 1885, 18, 3081), by the action of benzoic chloride on amarine-silver suspended in benzene. This method is, however, rather troublesome, and we found that the use of amarine-silver was unnecessary, provided that amarine and benzoic chloride were employed in the proportions required by the equation:



Cold benzene solutions of 10 grams of amarine and 2.3 grams (just under the theoretical proportion, so as to prevent all chance of the formation of the additive compound, benzoylamarine-benzoic chloride) of benzoic chloride were rapidly mixed, and after standing, the precipitated amarine hydrochloride was filtered off and extracted with boiling benzene. The united benzene solutions, on evaporating to dryness, gave crystals of benzoylamarine. By recrystallisation, first from ether, which removed some insoluble matter, and afterwards from benzene, the substance was obtained in almost rectangular tables, melting at  $179^\circ$  ( $180^\circ$ , Claus and Scherbel). In preparing and purifying this compound, hydrolytic solvents must be avoided, as they convert it into insoluble dibenzoyl-i-diphenylethylenediamine (see later on).

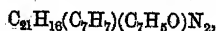
0.2062 gave 0.6324  $\text{CO}_2$  and 0.1059  $\text{H}_2\text{O}$ .  $\text{C} = 83.64$ ;  $\text{H} = 5.70$ .

0.2003 „ 11.95 c.c. moist nitrogen at  $12^\circ$  and 744 mm.  $\text{N} = 693$ .

$\text{C}_{28}\text{H}_{22}\text{ON}_2$  requires  $\text{C} = 83.58$ ;  $\text{H} = 5.47$ ;  $\text{N} = 6.97$  per cent.

Claus and Scherbel (*loc. cit.*), whilst adopting this formula, calculate for it the totally erroneous percentage composition  $\text{C} = 64.54$ ;  $\text{H} = 4.38$ ;  $\text{N} = 5.57$ . They publish, however, a full analysis, the results of which— $\text{C} = 64.50$ ;  $\text{H} = 4.52$ ;  $\text{N} = 5.30$ —are in agreement with their supposed theory.\* We therefore considered it necessary to

\* This is not the only case of the kind in Claus and Scherbel's paper. In the analysis of a compound which they describe as *benzylbenzoylamarine*,



they calculate the theoretical percentages:  $\text{C} = 83.0$ ;  $\text{H} = 5.13$ ; and find in accord.

make the foregoing analysis. In spite of their figures, the compound has the formula which they assign to it.

*Hydrolysis of Benzoylamarine to s-Dibenzoyl-i-diphenylethylenediamine.*—We observed that when benzoylamarine was boiled for some time with ordinary (that is, not absolute) alcohol the solution gradually became turbid owing to the separation of microscopic needles of an insoluble substance. Suspecting that a hydrolysis was taking place, we added a little concentrated hydrochloric acid to the solution; on boiling, the separation of the insoluble substance was very rapid, the reaction being complete in a few minutes. Addition of acetic acid had the same effect, but the action was slower.

The compound is identical with Grossmann's *s-dibenzoyl-i-diphenylethylenediamine* (dibenzoylstilbenediamine, *Ber.*, 1889, 22, 2300), some of which we prepared for comparison. The details of this comparison will be found in the next section of this paper, in connection with the supposed dibenzoylamarine, which is in reality the same substance.

The mechanism of the process by which the compound is formed from benzoylamarine is given in the introduction.

Nitrogen was determined in a specimen prepared by the action of alcohol acidified with hydrochloric acid on benzoylamarine.

0.1990 gave 11.80 c.c. moist nitrogen at 14° and 733 mm.  $N = 6.73$ .

$C_{28}H_{24}O_2N_2$  requires  $N = 6.67$  per cent.

A full analysis of the compound, formed in what is practically the same reaction, is given in the next section.

*The Supposed Dibenzoylamarine—s-Dibenzoyl-i-diphenylethylenediamine.*—By the action of benzoic chloride on amarine dissolved in ether, employing equimolecular proportions, Bahrman (*J. pr. Chem.*, 1883, [ii], 27, 300) obtained a substance which he regarded as "amarine-benzoic chloride,"  $C_{21}H_{18}N_2 \cdot C_6H_5 \cdot COCl$ , but which Claus and Scherbel (*Ber.*, 1885, 18, 3083) consider to be a mixture of benzoylamarine-benzoic chloride,  $C_{21}H_{17}(C_6H_5 \cdot CO)N_2 \cdot C_6H_5 \cdot COCl$ , with amarine-hydrochloride. As Bahrman showed, this substance dissolves in cold alcohol, but on standing, the solution becomes turbid from the separation of minute white needles of a substance free from chlorine, practically insoluble in ordinary solvents, and unaffected by acids and alkalis. Bahrman also obtained this insoluble compound direct by the action of benzoic chloride on amarine in alcoholic solution. He

dance with this,  $C = 82.7$ ;  $H = 5.6$  (*Ber.*, 1885, 18, 3084). The correct theory for this formula is, however,  $C = 85.36$ ;  $H = 5.69$ .

On the same page, they describe an isomeric *benzoylbenzylamarine*, and later on, in their theoretical discussion, they lay some stress on this isomerism. Yet the former compound, to judge from their analysis, has not the formula which they assign to it, whilst the latter does not appear to have been analysed at all. (Compare also the case of the supposed dibenzoylamarine, referred to later on,

analysed it (*loc. cit.*, 302) with the following results: C = 80.01, 79.99, 80.4; H = 6.13, 6.21, 6.28; N = 6.6 per cent. From these figures, he deduced the formula,  $C_{30}H_{26}O_2N_2$ , which requires C = 80.71; H = 5.84; N = 6.27 per cent., regarding the compound as amarine in which two atoms of hydrogen have been replaced by benzoyl and ethoxyl:  $C_{21}H_{16}(C_6H_5 \cdot CO)(OC_2H_5)N_2$ .

Claus and Scherbel (*loc. cit.*) repeated the above experiment, merely substituting benzene for ether as a solvent, and on decomposing the product with alcohol obtained the same insoluble substance. They obtained it also by boiling their benzoylamarine-benzoic chloride with alcohol. They publish the analytical figures: C = 82.90; H = 5.23,\* from which they conclude that the substance is dibenzoylamarine,  $C_{21}H_{16}(C_6H_5 \cdot CO)_2N_2$ , which requires C = 83.00; H = 5.13 per cent.

Claus and Scherbel's figures, it will be seen, differ considerably from Bahrman's, but the latter, although their author deduced from them a wrong formula, have the merit of accurately representing the composition of the substance, which, as the following comparison and analyses show, is Grossmann's *s-dibenzoyl-i-diphenylethylenediamine* already referred to. We prepared specimens by the four following methods:

1. By decomposing the product of the interaction of equimolecular proportions of benzoic chloride and amarine (benzoylamarine-benzoic chloride + amarine hydrochloride) with alcohol.
2. By the action of benzoic chloride on amarine in alcoholic solution.
3. By boiling monobenzoylamarine with alcohol acidified with hydrochloric acid (*vide supra*).
4. By Grossmann's method (*loc. cit.*) of treating *i*-diphenylethylenediamine with benzoic chloride.

All four specimens displayed identical properties, agreeing with the descriptions given by previous authors. They were all insoluble in the ordinary solvents and melted above the range of the ordinary mercurial thermometer. (Claus and Scherbel give the melting point as 366°, determined by means of a mercurial thermometer filled with nitrogen; Bahrman does not give any melting point; Grossmann merely says of his compound that it melts very high). Under the microscope, they appeared as flat needles with parallel edges and, in polarised light, showed straight extinction.

None of the previous investigators had been able to recrystallise the compound.† We found, however, that it dissolved fairly readily in boiling phenol, and on pouring the solution into alcohol, separated

\* A second analysis: C = 82.88; H = 5.04, is given by Scherbel (*Inaugural-Disseration*, p. 25, Freiburg i. B., 1885).

† Bahrman, by allowing a solution of the compound in concentrated sulphuric acid to absorb moisture, obtained crystals, but they contained sulphur.

in a crystalline form. Preparations 1 and 4 were thus recrystallised and a careful examination of the products showed that they had not undergone any chemical change during this treatment, the only difference being that under the microscope the crystals appeared larger, so that their behaviour towards polarised light could be more clearly observed.

Preparation 1 was analysed, both in the original and in the recrystallised condition. The substance is difficult to burn. Other combustions were made in addition to those here given, but all showed more than the allowable deficit of carbon.

0.1285 gave 0.3735  $\text{CO}_2$  and 0.0724  $\text{H}_2\text{O}$ .  $\text{C} = 79.27$ ;  $\text{H} = 6.26$ .

0.1471 „ 0.4282  $\text{CO}_2$  „ 0.0765  $\text{H}_2\text{O}$ .  $\text{C} = 79.39$ ;  $\text{H} = 5.78$ .\*

0.2323 „ 12.90 c.c. moist nitrogen at  $15^\circ$  and 766 mm.  $\text{N} = 6.56$ .

0.1915 „ 10.85 c.c. „ „  $15^\circ$  „ 750 mm.  $\text{N} = 6.55$ .

$\text{C}_{28}\text{H}_{24}\text{O}_2\text{N}_2$  requires  $\text{C} = 80.00$ ;  $\text{H} = 5.71$ ;  $\text{N} = 6.67$ .

The compound is, therefore, *s-dibenzoyl-i-diphenylethylenediamine*,  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ . The mechanism of its formation has been discussed in the introduction.

Bahrman's analytical figures, already quoted, agree better with this formula than with that deduced by him.

Claus and Scherbel state that the compound is decomposed by boiling with alcoholic potassium hydroxide, or even with water, into amarine and benzoic acid. This is contrary to Bahrman's statement, the accuracy of which we can confirm, as the compound is absolutely stable under these conditions.

*Bahrman's Supposed Diacetylamarine—Acetylbenzoyl-i-diphenylethylenediamine.*—By the interaction of equimolecular proportions of acetic chloride and amarine dissolved in ether, Bahrman (*J. pr. Chem.*, 1883, [ii], 27, 298) obtained a product which he termed "amarine-acetic chloride" (according to Claus, a mixture of acetylamarine-acetic chloride,  $\text{C}_{21}\text{H}_{17}(\text{CH}_3 \cdot \text{CO})\text{N}_2$ ,  $\text{CH}_3 \cdot \text{COCl}$ , and amarine hydrochloride), which behaves like the corresponding benzoyl derivative, dissolving in alcohol in the cold, but speedily decomposing, especially on warming, the solution depositing microscopic needles of a substance free from chlorine, almost insoluble in alcohol and the other ordinary solvents, and unaffected by mineral acids. He gives the melting point as  $268^\circ$  (we find  $316^\circ$ ). From his analyses he deduced the formula of a diacetylamarine,  $\text{C}_{21}\text{H}_{16}(\text{CH}_3 \cdot \text{CO})_2\text{N}_2$ , although his values for nitrogen— $\text{N} = 7.79, 7.69$ —are too high for this formula, which requires  $\text{N} = 7.33$  per cent.

We prepared this compound according to the above method, and

\* Combustion II was made by Mr. A. N. Meldrum.

can confirm Bahrmann's statements as to its physical properties, except that we found the melting point, after merely boiling the substance with alcohol, at  $315^{\circ}$ , and after dissolving it in boiling phenol and precipitating with alcohol, at  $316^{\circ}$ . Purified by the latter method, it formed colourless, microscopic needles, somewhat larger than those of the crude substance. In this form, it was analysed. Like the corresponding dibenzoyl derivative, it was difficult to burn, and the analyses showed a similar deficit of carbon.

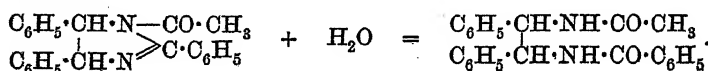
0.1587 gave 0.4444  $\text{CO}_2$  and 0.0906  $\text{H}_2\text{O}$ .  $\text{C} = 76.36$ ;  $\text{H} = 6.34$ .

0.1184 „ 0.3314  $\text{CO}_2$  „ 0.0695  $\text{H}_2\text{O}$ .  $\text{C} = 76.34$ ;  $\text{H} = 6.52$ .

0.1278 „ 8.75 c.c. moist nitrogen at  $16.3^{\circ}$  and 753 mm.  $\text{N} = 7.90$ .

$\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2$  requires  $\text{C} = 77.09$ ;  $\text{H} = 6.14$ ;  $\text{N} = 7.82$  per cent.

This is the formula of an *acetylbenzoyl-i-diphenylethylenediamine*, which would be formed from acetylamarine by hydrolytic opening of the ring :



### III. ISOAMARINE.

Isoamarine was isolated by Snape and Brooke (Trans., 1899, 75, 208) from the product of the action of heat on benzoylazotide, and to them is due the first detailed examination of this substance, although we shall show later on that it had been previously prepared by other investigators. It melts at  $198^{\circ}$ .

*Preparation of Isoamarine.*—We have found much simpler and more economical methods of preparing isoamarine than have hitherto been employed. The first of these was suggested by an accidental observation which we made in the course of the present work. In preparing dibenzylidene-*i*-diphenylethylenediamine by Grossmann's method, already referred to, of reducing amarine in boiling alcoholic solution with sodium, we on one occasion substituted amylic for ethylic alcohol, although Grossmann expressly states (*loc. cit.*) that the yield is thereby not improved. As a matter of fact, the yield was much worse; but we separated from the product a small quantity of a base crystallising in needles melting at  $197^{\circ}$ , which gave on analysis the following figures :

0.1676 gave 0.5144  $\text{CO}_2$  and 0.0967  $\text{H}_2\text{O}$ .  $\text{C} = 83.71$ ;  $\text{H} = 6.41$ .

0.2309 „ 19.05 c.c. moist nitrogen at  $14^{\circ}$  and 766 mm.  $\text{N} = 9.77$ .

$\text{C}_{21}\text{H}_{18}\text{N}_2$  requires  $\text{C} = 84.56$ ;  $\text{H} = 6.04$ ;  $\text{N} = 9.40$  per cent.

The agreement with the calculated composition is not good, but as we afterwards found, the substance was not quite pure. There could,



however, be little doubt that the compound was isomeric with amarine, and on comparing it with a specimen of isoamarine, for which we are indebted to Professor Snape, we could detect no difference between the two, except that our specimen melted  $1^{\circ}$  lower than the other, yielding a yellow instead of a colourless liquid.

As it appeared likely that the formation of this compound in the foregoing reaction was due to the direct action of the sodium on the amarine at the higher boiling point of the amylic alcohol, and not to the nascent hydrogen, we tried the effect of fusing amarine with sodium, and found that it was converted into a sodium derivative of *isoamarine*. The following method gave an excellent result.

Ten grams of amarine were melted in a large boiling tube heated in a spermaceti bath and kept at  $130^{\circ}$  until the water, which crystallised amarine almost invariably contains, was expelled. 0.8 gram of sodium was added, and the temperature was raised to  $190-200^{\circ}$ , shaking the tube so as to distribute the sodium. At this temperature, action took place, the sodium derivative of isoamarine solidifying on the walls of the tube. The product was dissolved in boiling benzene and filtered hot from any unaltered sodium; the filtrate almost solidified on cooling to a mass of needles of the sodium derivative, melting at  $205^{\circ}$ . When moistened, they show a strong alkaline reaction. They were dissolved in alcohol, and the solution was acidified with acetic acid, and then made alkaline with ammonia, when a crystalline deposit of practically pure isoamarine was obtained. A further quantity was obtained from the benzene mother liquor by the same process, the total yield being 5.5 grams. A portion, recrystallised from alcohol, melted at  $198.5^{\circ}$ . A little lophine was formed at the same time.

A still simpler method of preparing isoamarine consists in heating amarine hydrochloride at about  $340^{\circ}$  for 5 minutes, preferably in an atmosphere of gaseous hydrogen chloride, which checks the dissociation of the hydrochloride, thus diminishing, if not entirely preventing, the formation of lophine. The fused substance is thus, in great part, transformed into isoamarine hydrochloride. The product was dissolved in alcohol, and ether was carefully added as long as a crystalline precipitate of amarine hydrochloride was produced. As soon as an oil (isoamarine hydrochloride) began to separate, the solution was filtered; on evaporating to dryness, it gave a resinous mass of almost pure isoamarine hydrochloride, from which the base was obtained by dissolving the hydrochloride in hot alcohol and adding ammonia. On cooling, only isoamarine crystallised out, any amarine remaining in solution.

The mixed hydrochlorides may also be separated by boiling the powdered crude product with acetone, in which isoamarine hydrochloride is readily, amarine hydrochloride only sparingly, soluble. If

the mixture is cooled and allowed to stand before filtering, any amarine hydrochloride that may have dissolved is re-deposited.

*Molecular Weight of Isoamarine.*—The higher melting point of isoamarine as compared with that of amarine, and its more sparing solubility in alcohol, rendered it possible that it might be a polymeride of the latter compound. The molecular weight was therefore determined by Walker and Lumsden's modification of Landsberger's boiling point method, using alcohol (constant = 1560) as a solvent.\*

Substance.	Elevation.	Volume.	Mol. wt.
0.965	0.295°	14.7 c.c.	347
„	0.195	22.3	346
$C_{21}H_{18}N_2 = 298.$			

Isoamarine is therefore isomeric—not polymeric—with amarine.

*Reduction of Isoamarine by Sodium in Boiling Alcohol.*—In this experiment, we followed the method employed by Grossmann (*Ber.*, 1889, 22, 2298) in reducing ordinary amarine, except that we used a much larger proportion of sodium. 10 grams of isoamarine were dissolved in absolute alcohol, and about 30 grams of sodium cut into slices were added to the boiling solution. The product was diluted with water and most of the alcohol expelled on the water-bath; a yellow oil separated, more of which was obtained from the supernatant liquid by extraction with ether. This oil, which showed no tendency to crystallise, was boiled with dilute sulphuric acid, when it dissolved, benzaldehyde at the same time separating, recognisable by its smell. This showed that, as in Grossmann's analogous experiment, a benzylidene derivative—in this case doubtless Feist and Arnstein's dibenzylidene-*r*-diphenylethylenediamine (*Ber.*, 1895, 28, 3179), corresponding with Grossmann's meso-compound—had been formed in the reduction. The benzaldehyde and resinous matters were removed by extraction with ether, and the aqueous solution, which contained the sulphate of a base, was made alkaline with sodium hydroxide, and the organic base extracted with ether. On concentrating the ethereal solution, a small quantity of another basic substance, consisting of yellowish, silky needles melting at 242°, also observed by us in the reduction of ordinary amarine with sodium in boiling amylic alcohol, separated; it gives a blue coloration with concentrated sulphuric acid, and is, therefore, neither lophine nor tetraphenylazine. The quantity was insufficient for further examination. The ethereal filtrate from these needles was dried with fused potassium carbonate and then saturated with dry carbon dioxide, as described by Feist in his method for the preparation of *r*-diphenylethylenediamine (*Ber.*, 1894, 27, 215). A very bulky, almost gelatinous carbamate of the base separated; on

\* We are indebted to Mr. A. N. Meldrum for this determination.

filtering off and drying, it formed hard lumps, as described by Feist. It was yellow, but the colouring matter was removed by washing it with benzene.

For comparison, we prepared *r*-diphenylethylenediamine by Feist's method (*loc. cit.*) by the reduction of  $\alpha$ -benzildioxime, and converted it into its carbamate. Both carbamates had precisely the same appearance; both melted at 130–133° with evolution of gas, previously softening and caking together at 106° (Feist gives 106° as the melting point of the carbamate).

Various salts were prepared from the two carbamates and carefully compared. They showed absolute identity in their properties.

The *hydrochloride* formed prismatic needles melting in both cases at 253–254° (Feist gives 248°).

The *picrate* formed microscopic, orange-yellow needles melting in both cases at 220°, agreeing with Feist's determination.

The *dibenzoyl* derivative was prepared from the carbamate of the base obtained from isoamarine. The carbamate was treated with benzoic chloride by the Schotten-Baumann method, and the product purified by boiling it with alcohol. It formed a chalky, white powder melting at 286–287°, which agrees with Feist and Arnstein's determination.

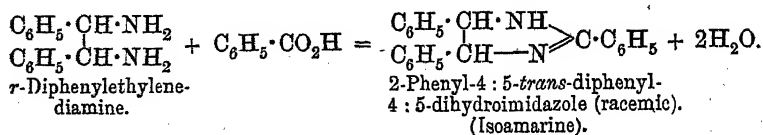
0.3342 gave 19.10 c.c. moist nitrogen at 15° and 767 mm.  $N = 6.75$ .

$C_6H_5 \cdot \underset{\text{CH} \cdot \text{NH} \cdot \text{CO} \cdot C_6H_5}{\text{CH} \cdot \text{NH} \cdot \text{CO} \cdot C_6H_5}$  requires  $N = 6.67$  per cent.

The free base is somewhat difficult to purify, and, with the small quantity at our disposal, we were unable to examine it in the case of the product from isoamarine. The foregoing results, however, suffice to prove that *r*-diphenylethylenediamine may be obtained from isoamarine by the process of reduction which, when applied to ordinary amarine, yields *i*-diphenylethylenediamine.

*Synthesis of Isoamarine.*—The carbamate of Feist's *r*-diphenylethylenediamine, prepared from  $\alpha$ -benzildioxime, was carefully heated with excess of benzoic acid until all the carbon dioxide was expelled, after which the temperature was raised to 180°, and kept there for 15 minutes. A slow evolution of gas (? aqueous vapour) was observed. The resinous product was dissolved in alcohol and ammonia added, when light brown needles, melting at 194°, and resembling isoamarine, separated. They were redissolved in alcohol, a little lophine remaining undissolved. On concentrating the solution and adding a trace of isoamarine crystals, a characteristic crystallisation of isoamarine instantly followed. The colourless needles thus obtained melted at 197–198° and were indistinguishable from Snape and

Brooke's compound. Isoamarine is here formed according to the equation



It might be objected that, in the foregoing synthesis, amarine was possibly the primary product, its benzoate afterwards changing, at the high temperature, into the isoamarine salt, as in the case of amarine hydrochloride already described. We therefore prepared amarine benzoate, which forms lustrous needles melting at 168°, and heated it at 180° as in the preceding experiment; but practically the whole of it was recovered unchanged, and no isoamarine was formed.

We tried, in like manner, to synthesise ordinary amarine by heating *i*-diphenylethylenediamine (m. p. 120–121°) with excess of benzoic acid; but even at 210° the desired reaction did not take place, and only *i*-diphenylethylenediamine dibenzoate (m. p. 206°) was obtained.

*Feist and Arnstein's Isoamarine.*—As already mentioned, Feist and Arnstein (*Ber.*, 1895, 28, 3177) claim to have obtained, by heating *s*-dibenzoyl-*r*-diphenylethylenediamine at 260° in a current of gaseous hydrogen chloride, an isoamarine structurally identical with the foregoing, but melting at 175°. As the existence of such a compound appeared to contradict the results which we had obtained, and to be incompatible with the views which we had formed as to the constitution of amarine and isoamarine, we repeated Feist and Arnstein's experiment. There was less blackening during the heating than their description would suggest. The liberated base, purified by crystallisation from alcohol, formed colourless needles melting at 198° (instead of at 175°), and was absolutely identical with Snape and Brooke's isoamarine.\*

The compound is so easy to purify that the wrong melting point given by Feist and Arnstein is doubtless a mere inadvertence.

*Isoamarine from Hydrobenzamide Hydrochloride.*—The observation that amarine hydrochloride is transformed on heating into isoamarine hydrochloride, led us to consider whether the latter compound might not also be obtained by the action of heat on dry hydrobenzamide hydrochloride—a reaction studied many years ago by Ekman (*Annalen*, 1859, 112, 151). Our supposition was that amarine hydrochloride

\* Snape and Brooke (*Trans.*, 1899, 75, 208), probably misled by the supposed difference in the melting points, state that the two compounds are distinct.

would be formed in the first instance, and would afterwards undergo the foregoing transformation.

On looking through Ekman's paper, we found a base described, which, both in composition and in properties, agreed so closely with isoamarine, that we had little doubt as to its identity with that substance. Ekman says (*loc. cit.*, 169): "This base is fairly soluble in cold alcohol, more readily in hot, and is deposited in obliquely truncated needles, arranged in stars. The needles are thicker, shorter, and better formed than those of lophine, and have a stronger, but not silky, lustre. The alcoholic solution has a strong alkaline reaction." He gives the melting point as  $200^{\circ}$ , and assigns the formula  $C_{21}H_{20}N_2$  to the compound, although his analyses agree, on the whole, rather better with the formula of isoamarine,  $C_{21}H_{18}N_2$ .

In repeating Ekman's experiment, we deviated somewhat from the conditions adhered to by him. He complains of the difficulty of saturating solid hydrobenzamide with gaseous hydrogen chloride, and we therefore dissolved the hydrobenzamide in benzene, dried the solution with ignited potassium carbonate, and, having transferred it to a distilling flask, saturated it with dry gaseous hydrogen chloride. This produced a sticky precipitate of hydrobenzamide hydrochloride. The benzene was distilled off in a current of the same gas, after which the temperature was gradually raised to  $240^{\circ}$ , and kept there as long as a liquid distillate (which smelt of benzonitrile and benzoic chloride) passed over. The current of hydrogen chloride was continued during the entire heating and subsequent cooling, as prescribed by Ekman. The brown resinous mass remaining in the distilling flask was disintegrated with boiling alcohol, which left a crystalline residue ( $\alpha$ ); and the alcoholic extract—which would contain the hydrochlorides of amarine, isoamarine, and lophine—was precipitated with water. The viscous precipitate was rejected, as the isoamarine hydrochloride would remain in the aqueous-alcoholic filtrate. From this filtrate, ammonia precipitated a mixture of bases, which was dissolved in hot alcohol; on cooling, lophine was deposited. The mother liquor from the lophine was acidified with hydrochloric acid and evaporated to dryness, and the residue was extracted with water, which dissolved isoamarine hydrochloride. By again evaporating to dryness and extracting with water, the isoamarine hydrochloride was obtained nearly pure. The isoamarine, liberated by ammonia and recrystallised from alcohol, formed obliquely truncated needles melting at  $197.5^{\circ}$ , and was indistinguishable from Snape and Brooke's compound. The yield was only about 2 per cent. of the hydrobenzamide taken.

Kühn, who repeated Ekman's experiments, obtained the same base (*Annalen*, 1862, 122, 322), but his work is less accurate than that of his predecessor. He gives the melting point as  $190^{\circ}$ . He

also adopts the formula  $C_{21}H_{20}N_2$ , although his figures, like those of Ekman, agree on the whole better with the formula  $C_{21}H_{18}N_2$ .

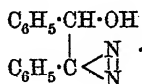
We were concerned only with the formation of isocamarine in the foregoing reaction, and did not endeavour to check the numerous other details of Ekman's work. We may mention, however, that the residue (a) from the extraction of the fused mass with alcohol, which Ekman asserts to be a non-basic isomeride of lophine, and Kühn to be lophine itself (he does not appear to have noticed Ekman's statement that it is non-basic), consists mainly of *tetraphenylazine*,  $C_{28}H_{20}N_2$ . It is mixed with another non-basic substance—possibly *kyaphenine*—of almost the same solubility, which lowers its melting point. We succeeded, however, in obtaining it with the correct melting point of  $245^\circ$ , and it was further identified by the magnificent red coloration which it yields with concentrated sulphuric acid.

#### IV. ACTION OF NITROUS ACID ON GROSSMANN'S DIPHENYLETHYLENE-DIAMINE (m. p. $120-121^\circ$ ).

After Feist and Arnstein had effected the separation of *r*-diphenylethylenediamine into its enantiomorphs (*Ber.*, 1895, 28, 3169), they studied the action of nitrous acid on it, in order to convert it into the corresponding  $\alpha\beta$ -diphenylglycol, and in this way to ascertain which of the two known  $\alpha\beta$ -diphenylglycols was the racemic form. The chief product of the reaction was diphenylacetaldehyde,  $(C_6H_5)_2CH \cdot CHO$ , formed from the expected  $\alpha\beta$ -diphenylglycol by elimination of water and simultaneous migration of a phenyl group; but, under special conditions, they succeeded in obtaining in small quantity, as an intermediate product, Erlenmeyer, jun.'s, isodiphenylhydroxethylamine (m. p.  $129-130^\circ$ ), and, as final product, isohydrobenzoin. They therefore regarded the latter substance as the racemic (in reality, *d+l*)  $\alpha\beta$ -diphenylglycol, as had already been proved by Erlenmeyer, jun., by resolving it into its enantiomorphs.

Erlenmeyer, jun. (*Annalen*, 1899, 307, 129), studied in great detail the action of nitrous acid on his isodiphenylhydroxethylamine. He obtained, as chief product, isohydrobenzoin; but a little hydrobenzoin was also formed, together with a considerable quantity of diphenylacetaldehyde. From these results, he concluded (*loc. cit.*, 111) that *r*-diphenylethylenediamine, isodiphenylhydroxethylamine, and isohydrobenzoin belong to the same series. The conclusion, however, so far as regards isodiphenylhydroxethylamine, appeared to be invalidated by his observation that Goldschmidt and Polonowska's diphenylhydroxethylamine (m. p.  $163^\circ$ ), when treated with nitrous acid, also yielded chiefly isohydrobenzoin (*loc. cit.*, 136), and he therefore admits the uncertainty of determinations of configuration in which

the replacement of the amino-group by hydroxyl by means of nitrous acid is employed. To account for the migrations which occur in such cases, he adopts Tafel's suggestion that an intermediate compound of the diazo-methane type is formed—thus, in the case which he is discussing,



The asymmetry of the carbon atom thus affected temporarily disappears, and does not re-appear until the diazo-group is replaced by hydrogen and hydroxyl, a process which may occur in two ways, yielding, in the one case, hydrobenzoin, in the other, isohydrobenzoin. The view that such an intermediate diazo-compound is formed receives support from the fact that, in the cold, the evolution of nitrogen is exceedingly slow.

Our study of the action of nitrous acid on the diphenylethylenediamine melting at 120—121° has convinced us that Erlenmeyer, jun.'s, doubts as to the admissibility of evidence drawn from the diazo-reaction in deciding questions of configuration, are entirely justified. Thus, as already mentioned, although we obtained, as final product, the expected hydrobenzoin (along with, apparently, a little isohydrobenzoin), the intermediate product was isodiphenylhydroxethylamine. The latter compound must therefore have been converted, in our reaction, chiefly into hydrobenzoin, whereas in the reactions studied by Feist and Arnstein, and by Erlenmeyer, jun., it yielded chiefly isohydrobenzoin. It is probably largely a question of the conditions under which the reaction is carried out which of the two configurations is obtained. Although, therefore, our experiments do not furnish any clue to the configuration of Grossmann's diphenylethylenediamine, we nevertheless describe them, as they may be of use to chemists engaged in studying the conditions under which these reactions may be expected to yield consistent results.

One gram of diphenylethylenediamine (m. p. 120—121°) prepared by Grossmann's method (*Ber.*, 1889, 22, 2298) was dissolved in hydrochloric acid, and to the dilute solution, previously cooled by ice, a solution of 0.7 gram of sodium nitrite was added. Beyond the production of a faint turbidity, there was no visible effect. The solution was therefore heated on the water-bath until the evolution of nitrogen ceased. The solution was still practically clear; but on testing a portion with ammonia, crystals melting at 127° separated; these we show later on to be isodiphenylhydroxethylamine (m. p. 129—130°). As the reaction had, therefore, gone only half way, excess of sodium nitrite was added, and the solution was again heated at 100°. From the cooled

liquid, ether extracted the non-basic product, which, on expelling the ether, remained as an oil; but on adding ammonia to the aqueous solution and again extracting with ether, a basic product was obtained, showing that the second amino-group is attacked only with difficulty.

The non-basic portion was dissolved in a little benzene, and light petroleum added. Small oblique plates separated, melting at  $131^{\circ}$  (m. p. of hydrobenzoin  $134^{\circ}$ , Forst and Zincke;  $138^{\circ}$ , Paal). The substance was not homogeneous, and as the quantity was too small for purification, we warmed it with benzoic chloride and caustic soda, hoping to be more successful in isolating the sparingly soluble dibenzoate. The product, extracted with hot alcohol, left a residue melting at  $245^{\circ}$  (m. p. of hydrobenzoin dibenzoate,  $247^{\circ}$ ). There were indications of the presence of a benzoate of isohydrobenzoin; but the quantity was too small for identification.

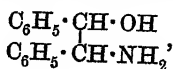
Although we were unable to analyse the substance, it is tolerably evident, from the foregoing, that *hydrobenzoin*, and not isohydrobenzoin, was the chief product of the action of an excess of nitrous acid on Grossmann's diphenylethylenediamine.

In order to obtain the intermediate, basic product, 2 grams of Grossmann's dibenzylidene-diphenylethylenediamine were hydrolysed with dilute sulphuric acid, removing the liberated benzaldehyde by ether. To the acid solution of the diphenylethylenediamine sulphate thus obtained,\* 0.75 gram of sodium nitrite was added, and the mixture was heated on the water-bath. This time, ether extracted only a trace of non-basic substance; but on adding ammonia and again extracting, a good yield of the basic product was obtained. It was twice crystallised from benzene, from which it separated in rosettes of short prisms, melting at  $125^{\circ}$ . This agrees with the description of isodiphenylhydroxethylamine, except that the latter melts at  $129-130^{\circ}$ , although only after repeated crystallisation from benzene. Further purification would not have left enough for analysis.

0.1364 gave 7.60 c.c. moist nitrogen at  $18.2^{\circ}$  and 767 mm.  $N = 6.50$ .

$C_{14}H_{15}ON$  requires  $N = 6.57$  per cent.

The compound is therefore *isodiphenylhydroxethylamine*,



as the stereoisomeric diphenylhydroxethylamine melts at  $163^{\circ}$ .

The *platinichloride* was prepared. It crystallised in rhombs, frequently forming aggregates of overlapping crystals ("treppenförmige

\* This method was adopted in order to avoid the loss involved in isolating the base.



Aggregate"), as described by Söderbaum (*Ber.*, 1895, 28, 2523). It melted at 226°, previously turning grey at 215°. (Söderbaum gives 213° as the melting point).

These experiments on the action of nitrous acid on Grossmann's diphenylethylenediamine are unsatisfactory, as the quantities of substance employed were too small to allow of the thorough purification of the products, not to speak of the isolation of the bye-products. They were intended to be merely provisional; but when we found that they would not solve the problem of the configuration of Grossmann's base (as was evident from the fact that both *r*-diphenylethylenediamine and what must be regarded as *i*-diphenylethylenediamine give, in the first stage of the reaction, *isodiphenylhydroxethylamine*) we did not trouble to repeat them on a larger scale.

Our present knowledge of the stereochemical relationship of the  $\alpha\beta$ -diphenylethylenediamines, the  $\alpha\beta$ -diphenylhydroxethylamines, and the  $\alpha\beta$ -diphenylglycols to one another may be summed up as follows. Feist's *r*-diphenylethylenediamine (m. p. 90—92°) and *isohydrobenzoin* undoubtedly possess corresponding configurations, as each has been resolved into its enantiomorphs. The related *meso*-configurations must therefore be assigned to Grossmann's diphenylethylenediamine (*i*-diphenylethylenediamine, m. p. 120—121°) and *hydrobenzoin* respectively. As regards the two intermediate compounds, *isodiphenylhydroxethylamine* and *diphenylhydroxethylamine*—each an enantiomorphous pair not yet separated into its dextro- and lævo-components—their position must, for the present, be regarded as uncertain. Erlenmeyer, jun.'s, suggestion that *isodiphenylhydroxethylamine* is the intermediate stage between *r*-diphenylethylenediamine and *isohydrobenzoin* is probably correct: not, however, for the reason which he assigns (*vide supra*), inasmuch as the evidence of the diazo-reaction is obviously untrustworthy, but because of the parallelism in the melting points of the two following series:

	M. p.		M. p.
<i>r</i> -Diphenylethylenediamine...	90—92°	<i>i</i> -Diphenylethylenediamine...	120—121°
<i>Isodiphenylhydroxethylamine</i>	129—130	<i>Diphenylhydroxethylamine</i> ...	163
<i>Isohydrobenzoin</i> .....	119	<i>Hydrobenzoin</i> .....	134

The analogy of the melting points must not, however, be pushed too far.

We desire to express our indebtedness to the Council of the Royal Society for a grant from the Government Grant Fund, by which part of the expense of the present work has been defrayed.

CHEMICAL DEPARTMENT,  
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## LII.—*Vapour Density of Dried Mercurous Chloride.*

By H. BREBETON BAKER, M.A.

AMONG the large number of changes for which the presence of moisture is necessary, only one case of dissociation has been studied, that of ammonium chloride (Trans., 1894, 65, 615; 1898, 73, 422). Since this substance has a normal density when dried, it was thought that others, which have abnormal densities, might give interesting results if they were converted into vapour after careful drying.

Mercurous chloride was selected as a suitable substance, since its dissociation under ordinary circumstances is well established. It was obtained in a sufficiently pure condition by the following method.

Mercury was purified by shaking for 3 days with dilute nitric acid, then washed, boiled and distilled twice in a nitrogen vacuum. It was dissolved in cold nitric acid and precipitated with hydrochloric acid. The precipitated mercurous chloride was washed without contact with filter paper, until a large quantity of the wash-water gave, on evaporation, no opalescence with silver nitrate. It was dried at  $110^{\circ}$  and kept in a desiccator in a dark cupboard.

The vapour density determinations were made by Victor Meyer's method in an apparatus constructed of hard glass. A bent tube, in which plugs of phosphoric oxide were placed, was ground to fit the neck of the apparatus.

A small, hard glass tube containing a known weight of the substance rested on a glass spoon, the shaft of which was ground into a side tube fused to the neck of the apparatus. By turning the shaft of the spoon which projected from the side tube, the substance could be made to fall into the bulb of the apparatus. The whole apparatus was heated to low redness, while a current of nitrogen, dried by sulphuric acid, was passed through it, the delivery tube being then sealed. The tube containing mercurous chloride was then introduced, and the phosphoric oxide tube, previously filled with nitrogen, was put into position. No lubricators were used; mercury seals being placed over the two ground joints. The closed apparatus was left in the dark for three weeks. The bath used was an iron tube surrounded by a fireclay cylinder. In this, sulphur was boiled.\* The delivery

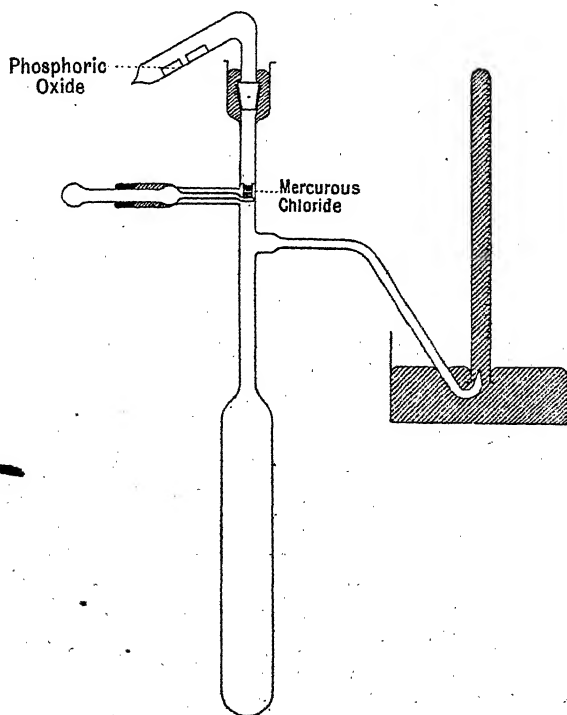
\* The actual determinations were performed almost in the dark, and this led to the observation of a phenomenon of which I can find no previous record. When the glass bulb was removed from the heated bath after the experiment, the sulphur burnt with a luminous, blue glow, very similar in character to the glow of phosphorus in air. If allowed to continue, this glow changes into the ordinary flame of sulphur. I have failed to reproduce this phenomenon in oxygen at the ordinary pressure, but it is distinctly seen in this gas at about half the atmospheric pressure.

tube dipped into a trough containing mercury which had just been boiled. The point of the delivery tube was not broken until there was a considerable excess of pressure in the apparatus, so as to diminish the chance of moisture diffusing from the dried mercury into the bulb.

The results of the determinations of the vapour density were :

I.	II.	III.	IV.	V.	Mean.
217.7	222.8	221.3	223.9	201.4	217.4
Calculated for no dissociation.....					235

A similar experiment, conducted in nitrogen which had been dried only by sulphuric acid, gave a vapour density of 118.4. Hence the



dissociation of mercurous chloride is much hindered by removing moisture as far as possible.

Some confirmation of this result was obtained by heating in the same air-bath the purified mercurous chloride in a nitrogen vacuum in two tubes containing gold leaf, one dried by phosphoric oxide, the other not specially dried. No amalgamation of the gold was seen in the dried tube, whilst in the other the gold had been freely attacked.

Similar vapour density determinations were made with metallic mercury in order to find out if the vapour, which is under ordinary circumstances monatomic, is a product of the dissociation of a more complex molecular structure. These experiments were conducted at the boiling point of sulphur, the mercury used being a portion of that from which the mercurous chloride was prepared. The densities obtained were :

I.	II.	III.	Mean.
107.6	104.4	112.5	108.1

The vapour of dried mercury is therefore probably monatomic.

Many experiments have been made with phosphorus pentachloride, but very great difficulties have been experienced in obtaining it in a sufficiently pure state for the purpose. Until recently, all the results pointed to complete dissociation having taken place. The last determination, however, with a new specimen of the purified pentachloride, gave, at 440°, a density of 89.2, that calculated for no dissociation being 104.2. Phosphorus pentachloride may therefore be ultimately shown to undergo no dissociation when dried before heating, if it is obtained in a sufficiently pure condition.

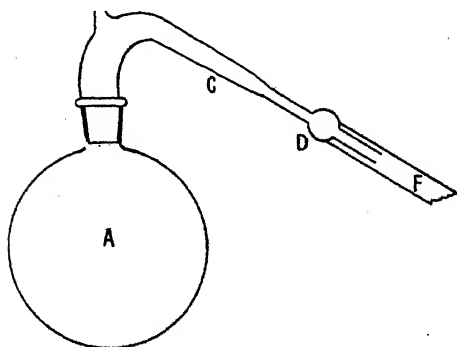
DULWICH COLLEGE.

### LIII.—*Preparation of Pure Hydrobromic Acid.*

By ALEXANDER SCOTT.

THE process for preparing pure hydrobromic acid "*destiné aux essais des matieres d'argent*," recommended by Stas (*Œuvres*, 1, 839), depends on the use of amorphous phosphorus as the agent for transforming the pure bromine into hydrobromic acid. Stas gives minute directions as to testing the phosphorus to be employed so as to ensure its entire freedom from the chlorides apt to be introduced with the alkali used in getting rid of any ordinary phosphorus: He has, however, quite overlooked an impurity in the phosphorus itself, one, indeed, which may be termed a normal impurity in all samples of phosphorus in the manufacture of which arsenical sulphuric acid has been employed. A moment's consideration shows that in the ordinary process of manufacturing phosphorus from phosphates, all the arsenic in the sulphuric acid employed will probably be found in the phosphorus obtained. When such phosphorus is treated with bromine, the arsenic is converted into arsenious bromide, which distils over with the hydrobromic acid, supposed to be of a very high degree of purity, and all bromides prepared with such acid are almost certain to be contaminated with arsenites and arsenates.

In preparing, some time ago, a fairly large quantity of hydrobromic acid, the phosphorus employed contained an extremely large amount of arsenic (over 1 per cent.); it was selected because it was a very old sample, and in a pasty (almost syrupy) condition from oxidation, and therefore very easily and satisfactorily washed free from chlorides. The hydrobromic acid when tested was found to give a very large precipitate of arsenious sulphide on treatment with hydrogen sulphide, and had to be diluted, treated with pure hydrogen sulphide (from zinc sulphide and dilute sulphuric acid), filtered, concentrated, and redistilled. No doubt in many cases the acid, after one or two distillations, would lose most of the arsenious bromide which it might contain, as this comes over largely in the first portions of the distillate, that is,



with water containing only small quantities of hydrobromic acid. But if the purest hydrobromic acid be desired, it is obviously much better to use materials as free from impurities as possible, rather than to trust to the purification of the acid afterwards.

An extremely convenient and satisfactory reducing agent to replace the phosphorus is found in liquid sulphur dioxide, which may be procured in glass syphons. This gives rise to no volatile bromides, and the hydrobromic acid is easily separated by distillation from the sulphuric acid produced at the same time. The apparatus required and its manipulation are of the simplest nature, and are almost sufficiently explained by the figure.

The bolt head with ground-in neck, or the distillation flask *A* has

sealed to its neck a glass tube, B, of such length and diameter that it will allow the thermometers usually employed to pass easily down into the wider part of the neck, and also to admit a tube through which the sulphur dioxide is to be passed. This tube or the thermometer employed is held air-tight in its place by a small piece of indiarubber tubing. The exit tube, C, has on it a bulb, D, of such a diameter that it is a little too large to pass into the inner tube, F, of a Liebig's condenser. If this inner tube has its end cut off quite square, and the sharp edges carefully taken off and nicely rounded by grinding it on a piece of not too rough emery paper held flat in the palm of the hand, we have, by bringing the bulb D into contact with the rounded edge, a joint which will allow of the distillation of litres of constant boiling point hydrobromic acid without any fuming, and with perfect security from any contamination by organic matter. The sulphuric acid obtained as a bye-product in the preparation of two or three kilograms of hydrobromic acid was distilled through a long tube simply air-cooled by means of this apparatus, without any inconvenience whatever from fumes.

To prepare a kilogram of real hydrogen bromide in solution, 350 c.c. of pure bromine are placed in A along with 2 litres of water, and a rapid current of sulphur dioxide washed first through a strong solution of sodium sulphite and then through water, is led *into the water* about 5 to 10 mm. above the surface of the bromine until the whole is transformed into a pale yellow, homogeneous liquid. Should the liquid become colourless, the yellow colour must be restored before distillation by the cautious addition of bromine or bromine water. This prevents any possible contamination of the hydrobromic acid with sulphurous acid, besides being a further security against traces of iodine or hydriodic acid occurring in the final product.

The acid is distilled from the vessel in which it is formed, and it is advantageous to keep a gentle current of air bubbling through the liquid throughout the distillation, as the troublesome bumping of the liquid is thus obviated. Practically the whole of the hydrogen bromide will have passed over when the residual sulphuric acid reaches the density 1.7. On redistilling, water comes over first, bringing with it all the free halogen, but only traces of acid.

When the acid begins to come over, the receiver is changed, and the acid should be once more redistilled from a small quantity of barium bromide to guarantee its freedom from every trace of sulphuric acid. This last distillation is best carried out with a very gentle current of hydrogen, which cannot be safely employed as long as the liquid to be distilled contains free sulphuric acid.

The purity of a sample of the acid prepared in this way was tested by preparing from it some potassium bromide, and titrating it against

silver with all the precautions described by Stas; the equivalent of this bromide was found to be 119.099 ( $Ag = 107.93$ ). A sample of bromide from the same specimen of pure potassium carbonate, and from the hydrobromic acid above referred to prepared by Stas's process, after being carefully freed from compounds of arsenic, gave an identical value 119.099, whilst another specimen of bromide, prepared from pure hydrobromic acid, made by Squibb's process, as recommended by J. P. Cooke (*Proc. Amer. Acad.*, 1881, 17, 31) gave the value 119.102.

The acid from which this last sample was prepared contained traces of platinum from having been distilled through a platinum condenser. This cannot be done with safety with hydrobromic acid in presence of atmospheric oxygen. Stas (*Œuvres*, 1, 748) gives the value 119.095 as the mean of 14 determinations of the equivalent of potassium bromide.

DAVY FARADAY RESEARCH LABORATORY  
OF THE ROYAL INSTITUTION.

#### LIV.—*A New Sulphide of Arsenic.*

By ALEXANDER SCOTT.

WHEN phosphoric acid is prepared by the oxidation of phosphorus by means of nitric acid, as is well known, the action takes place in two stages, which are more or less distinct according to the concentration of the nitric acid employed. Phosphorous acid is first produced, and if sufficient nitric acid be present, on boiling down the liquid, a point is reached when these react with some energy, giving rise to phosphoric acid with the production of torrents of red fumes. If, however, the nitric acid be not present in sufficient excess, the liquid almost invariably becomes brown in colour, and black flakes may even separate out. This is not due to the charring of any organic matter, but to the arsenic usually present in the phosphorus, which has been oxidised first to arsenic acid, and this, in turn, on concentration, is reduced again by the phosphorous acid present to arsenic. If sulphur dioxide be passed into the liquid before the second stage be reached and the solution warmed, a bright yellow precipitate of arsenious sulphide is obtained if arsenic be present, due to the reduction of the sulphurous acid to hydrogen sulphide, which then reacts with the arsenic or arsenious acid present. This reaction may be applied to the detection of arsenates or arsenites in solution, a solution containing 0.1 per cent. of arsenic acid giving an abundant precipitate of arsenious

sulphide, but if the solution of arsenic be very dilute, the reaction is apt to be masked by the simultaneous precipitation of sulphur. The easiest way to apply the test is to add about 1 c.c. of phosphorus trichloride to the solution to be tested, and warm after adding some sulphurous acid.

If, instead of heating the mixed solutions, they be allowed to stand at the ordinary temperature for some time, the solution becomes brown, and after about a day practically the whole of the arsenic is found as a dark brown precipitate. It was at first thought that this might be pure arsenic or arsenic mixed with sulphur, or with some sulphide of arsenic, or perhaps the brown or black substance obtained by Berzelius on treating realgar with potash solution and described by him as a sulphide of arsenic.

Analysis showed that it could not be this substance, as it contains about 13 per cent. of sulphur, whilst the black sulphide, according to Berzelius, contains only 3.44 per cent., corresponding to the formula  $As_{12}S$ .

The new sulphide is insoluble in solutions of either ammonia or colourless ammonium sulphide, but dissolves readily in yellow ammonium sulphide, which is at the same time decolorised, and from the solution arsenious sulphide is precipitated on the addition of excess of hydrochloric acid. Carbon disulphide removes no sulphur from it on treatment for many hours in a Soxhlet's extraction apparatus.

Analyses of samples prepared at various times and with varying quantities of the reagents gave the following results:

	I.	II.	III.	IV.	V.
Sulphur.....	12.7	13.09 (mean of four)	13.62	13.6	13.3
Arsenic.....	—	87.06* (mean of two)	—	86.1†	—

The percentage of sulphur is usually rather higher than 12.45, which is required by the formula  $As_3S$ , owing to the great difficulty of removing every trace of arsenious sulphide, which always accompanies it in small quantity. A quantity of sample II. above mentioned was treated with dilute ammonia solution on the water-bath, then a little hydrogen sulphide passed in and the digestion continued for some time, the liquid poured off, and the treatment repeated until the solution of ammonium sulphide thus prepared gave no yellow precipitate with excess of hydrochloric acid. On now analysing the residue, it was found to contain 12.3 per cent. of sulphur. A portion of this residue was now taken and treated with ammonia solution and hydrogen sulphide passed in, and one-eighth part of the sulphur required to

\* Estimated gravimetrically as magnesium pyroarsenate.

† Estimated volumetrically as arsenious acid with standard iodine solution (Szarvasy, *Ber.*, 1897, 29, 2900).



transform the sulphide into arsenious sulphide was added in fine powder, and, after digestion, the residue was collected and analysed, when it was found to contain 12.5 per cent. of sulphur; another portion was taken and similarly treated, but with twice the quantity of sulphur, and the residue from this analysed; it contained 12.3 per cent. of sulphur. This seems to prove conclusively that the substance behaves chemically as a single substance and not as a mixture. Heat resolves it into realgar, which sublimes, and arsenic, which remains behind. It is acted upon by potash solution, which leaves a substance of a darker colour containing 2.34 per cent. of sulphur.

Realgar was treated with potash in order to obtain the substance described by Berzelius. Commercial realgar containing 32.9 per cent. of sulphur ( $\text{As}_2\text{S}_2$  contains 30 per cent.) gave a dark-brown residue containing 4.33 per cent. of sulphur. Native realgar was distilled, and the dark brown residue remaining after treatment with potash of the realgar thus purified contained exactly 1.0 per cent. of sulphur.

Convenient quantities of materials for the preparation of the new sulphide are: 200 grams of crystallised sodium arsenate dissolved in  $3\frac{1}{2}$  litres of water, and then 150 c.c. of phosphorus trichloride added and allowed to stand till quite cold, the solution filtered and sulphur dioxide passed in and allowed to stand for a day or two. The supernatant liquid is then poured off and the precipitate washed first with water, then with dilute ammonia solution, then warmed with stronger solution of ammonia, and into this hydrogen sulphide is passed and the digestion continued for an hour or two; the precipitate is then well washed with water by decantation, and finally with alcohol, and dried in a vacuum. The same sulphide is obtained from arsenites, but the yield is much smaller in proportion, owing to the precipitation of much arsenious oxide from the strongly acid solution.

As solutions of antimony react but slightly with the solution of phosphorous and sulphurous acids, especially when warmed, and in presence of hydrochloric acid, it was hoped that conditions would be discovered under which arsenic and antimony might be quantitatively separated, but so far without success. The precipitates from the mixed solutions always contained notable quantities of antimony.

I have much pleasure in expressing my indebtedness to Mr. Wm. Arbuckle, assistant in the Davy Faraday Laboratory for making most of the careful analyses recorded above.

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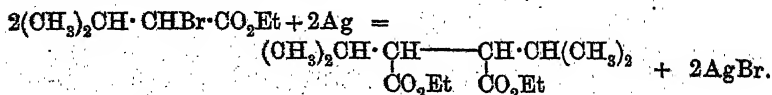
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LV.—*Researches on the Alkyl-substituted Succinic Acids. Part II. s-Dipropyl, s-Diisopropyl, and  $\alpha\alpha_1$ -Propylisopropyl-succinic Acids.*

By WILLIAM A. BONE and CHARLES H. G. SPRANKLING.

OF the acids which form the subject of this communication, only *s*-diisopropylsuccinic has been previously investigated, and our knowledge of it even has not only been incomplete, but in certain respects very unsatisfactory.

In 1889, Hell and Mayer (*Ber.*, 1889, 22, 48) obtained two crystalline dibasic acids of the formula  $C_{10}H_{18}O_4$ , melting at 168—169° and 199—200° respectively, by hydrolysing the oil obtained by the action of molecular silver upon ethyl  $\alpha$ -bromoisovalerate at a temperature of 150°. Both acids were sparingly soluble in cold water, and formed characteristic insoluble calcium, barium, and strontium salts; they could be separated by distillation with steam, for the acid of lower melting point formed a volatile anhydride, whereas the other was non-volatile, and moreover, did not give an anhydride when heated to a temperature of 210°. Hell and Mayer suggested that the acids might be the two stereoisomeric *s*-diisopropylsuccinic acids, formed from ethyl  $\alpha$ -bromoisovalerate, as follows:



Considering, however, that the action of molecular silver upon such  $\alpha$ -bromo-esters was known to be a somewhat complex one (compare V. Meyer and Auwers, *Ber.*, 1889, 22, 3005; 1890, 23, 295), and does not merely consist in the elimination of bromine and the coupling up of two residues, as indicated by the foregoing equation, they admitted the possibility of structural difference between the two acids, and even suggested that, whereas one of them was probably a *s*-diisopropylsuccinic acid, the other might be  $\alpha\alpha\alpha_1$ -tetramethyladipic acid.

In 1896, Auwers re-investigated the products of the same reaction (*Annalen*, 1896, 292, 162), but was quite unable to isolate more than one acid of the formula  $C_{10}H_{18}O_4$ . It melted at 178—182°, a temperature, it will be observed, intermediate between the melting points of the two acids obtained by Hell and Mayer; it was sparingly soluble in water, yielded a very stable and volatile liquid anhydride, and an anilic acid melting at 179—180°. He had no hesitation in pronouncing it to be a *s*-diisopropylsuccinic acid. As *s*-diisopropylsuccinic acid contains two asymmetric carbon atoms, and should, therefore, like other

symmetrically di-substituted succinic acids, exist in two inactive forms, Auwers tried to effect the conversion of his acid into a stereoisomeric form, by heating it in sealed tubes with water or hydrochloric acid at 180—200°, but was quite unsuccessful. On the results of these two or three isolated negative experiments, he felt justified in concluding that "*die symmetrische Diisopropylbernsteinsäure besteht im Gegensatz zu andern symmetrisch disubstituirten Bernsteinsäuren nur in einer Modification*" (the italics are his), and further that the acid possesses such peculiar properties, "dass die Existenz einer zweiten Modification dieser Säure als sehr unwahrscheinlich gelten muss. Jedenfalls müsste dieses hypothetische Isomere weit labiler sein, als alle bekannten stereoisomeren Dicarbonsäuren" (*ibid.*, 164 and 166). We shall have no difficulty in showing that his conclusions were ill-founded.

Auwers' acid possessed one remarkable property for an acid of the succinic series, namely, a high dissociation constant. Whereas this value for succinic acid itself is 0.0068, whilst those for its mono-alkyl derivatives vary between 0.0075 and 0.0088, and those for other *s*-dialkylsuccinic acids never exceed 0.0250, Auwers found that the value for his acid varied from 0.2047 to 0.3586, according to the concentration of the solution, thus :

I.			II.	
<i>c.</i>	$\mu_{90}$	100 <i>k.</i>	$\mu_{90}$	100 <i>k.</i>
256	211.2	0.3586	—	—
512	247.0	0.3302	248.7	0.3407
1024	275.2	0.2815	278.9	0.3004
2048	291.9	0.2047	301.1	0.2584
		0.2938		0.2998

It is difficult to reconcile these results with the supposition that the acid under examination was a homogeneous substance, for, of course, the constant of a pure acid is independent of the dilution. Auwers did, indeed, for this very reason, suspect "dass die sorgfältig gereinigte Säure doch ein Gemisch von zwei Stereoisomeren sei, die durch fractionirte Krystallisation nicht zu trennen seien," but a further study of the acid convinced him that there was no ground for any such suspicion.

Some months ago (*Trans.*, 1899, '75, 839), we described a new method for preparing alkyl-substituted succinic acids in quantity from ethyl cyanoacetate; we determined to synthesise *s*-diisopropylsuccinic acid by means of it, in order to obtain further evidence as to its stereochemical character. We were also led to prepare and examine the hitherto unknown *s*-dipropyl- and *aa*<sub>1</sub>-propylisopropyl-succinic acids.

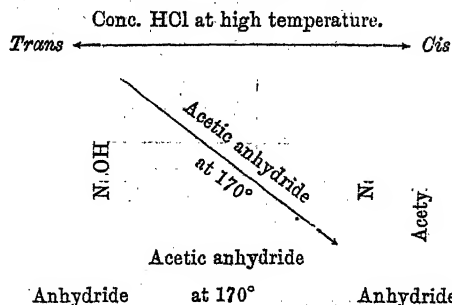
Ethyl propylcyanosuccinate and isopropylcyanosuccinate were prepared by the interaction of ethyl sodiocyanacetate and ethyl  $\alpha$ -bromovalerate or  $\alpha$ -bromoisovalerate respectively; the resulting oils were then propylated or isopropylated, as the case might be, in the usual manner. The propylated or isopropylated products were hydrolysed in two stages, namely, first by treatment with alcoholic potash, and then by heating the resulting mixture of acids with 50 per cent. sulphuric acid, in order to complete the hydrolysis of the cyano-group, and to ensure the total elimination of carbon dioxide from the resulting tri-carboxylic acid.\* The acid liquid was at once subjected to distillation with steam, when, in every case, a volatile anhydride passed over, leaving a non-volatile acid behind. Thus, in all three cases, we were able to obtain two different acids, which subsequent investigation proved to be stereoisomeric, being respectively the *cis*- and *trans*-modifications.

The six acids are all sparingly soluble in water, and yield characteristic, sparingly soluble calcium salts. The *trans*-acids are either quite insoluble, or only sparingly soluble, in benzene, whereas the *cis*-isomerides are all readily soluble in this solvent. All the acids yield their own liquid anhydrides on being heated with acetyl chloride, the *cis*-, however, much more readily than the *trans*-. These anhydrides are very stable substances, and are not decomposed to any appreciable extent by being boiled with water. They readily dissolve, however, in warm dilute sodium hydroxide, in each case forming the sodium salt of the acid from which the anhydride was originally derived: Each anhydride, with aniline, yields a characteristic anilic acid, and, except in the case of *cis*- $\alpha\alpha$ -propylisopropylsuccinic, these anilic acids are all solids.

When a mixture of *cis*- and *trans*-acids is dissolved in 50 per cent. sulphuric acid, and the solution subjected to distillation with steam, the *cis*-isomeride is converted into its anhydride, which is volatile, whereas the *trans*-acid remains behind unchanged. In this way, a quantitative separation of the two isomerides may be effected.

We have also shown that a *cis*- or *trans*-acid may be partly converted into the opposite isomeride by heating it with hydrochloric acid in sealed tubes at temperatures varying from 180° to 230°, and that, provided the time of heating be in either case sufficiently prolonged, the final state of equilibrium between the two isomerides is the same. The *trans*-acids or anhydrides are gradually but completely converted into the *cis*-anhydrides by boiling them with acetic anhydride. The mutual convertibilities of the stereoisomerides are shown in the following diagram:

\* The reasons for conducting the hydrolysis in two stages will be fully discussed later.



The melting points of the several acids and their anilic acids may be tabulated as follows :

	<i>Trans.</i>		<i>Cis.</i>	
	Acid.	Anilic acid.	Acid.	Anilic acid.
<i>s</i> -Dipropylsuccinic .....	182—183°	184—185°	121°	101—102°
<i>s</i> -Diisopropylsuccinic .....	226°	201—202°	171°	184—185°
<i>aa</i> <sub>1</sub> -Propylisopropylsuccinic	192—194°	147—149°	151—152°	liquid

We have also investigated the dissociation constants of each of the three pairs of acids. In the case of the *s*-dipropyl and *aa*<sub>1</sub>-propylisopropyl acids, the expected values were obtained, those of the *cis*-acids being approximately double those of the corresponding *trans*-isomerides. The presence of two isopropyl groups in the 'succinic' molecule, however, has an extraordinary influence upon the conductivity of the acids, the value for the *cis*-*s*-diisopropyl acid being much higher than has hitherto been observed in the case of any other member of the succinic series, and over twenty times as great as that of the *trans*-isomeride. These results are discussed at the end of this paper.

#### EXPERIMENTAL.

##### *A. Preparation of Ethyl β-Propylcyanosuccinate and β-Isopropylcyanosuccinate.*

The details of the operations involved in the preparation of ethyl β-propylcyanosuccinate and β-isopropylsuccinate by the interaction of ethyl sodiocyanoacetate and ethyl α-bromovalerate, or α-bromoiso-valerate respectively, are practically identical with those described in our previous paper in the case of ethyl ββ-dimethylcyanosuccinate (Trans., 1899, 75, 854). The yields of refractionated oils obtained

amounted to between 44 and 50 per cent. of those theoretically possible. The properties of the esters may be tabulated as follows:

	B. p. 19—21 mm.	$d_{4}^{0}$ .	$\mu_{Na}$ .
Ethyl $\beta$ -propylcyanosuccinate .....	171°	1.0638	1.4895
Ethyl $\beta$ -isopropylcyanosuccinate.....	165—167°	1.0620	1.4418

The oils were analysed with the following results:

*Ethyl  $\beta$ -Propylcyanosuccinate:*

0.1965 gave 0.4300  $\text{CO}_2$  and 0.1360  $\text{H}_2\text{O}$ . C=59.68; H=7.78.

0.2237 „ 11.2 c.c. nitrogen at 6° and 773 mm. N=6.15.

*Ethyl  $\beta$ -Isopropylcyanosuccinate:*

0.2270 gave 0.4951  $\text{CO}_2$  and 0.1618  $\text{H}_2\text{O}$ . C=59.62; H=7.92.

0.2548 „ 13.2 c.c. nitrogen at 5° and 762 mm. N=6.24.

$\text{C}_{12}\text{H}_{19}\text{O}_4\text{N}$  requires C=59.75; H=7.88; N=5.80 per cent.

In order to be quite sure that the oils just described had the constitutions assigned to them, we hydrolysed small portions of each with concentrated hydrochloric acid, and then isolated the resulting dicarboxylic acid by means of its sparingly soluble calcium salt. In each case, almost theoretical yields of one, and one only, of two acids were obtained, the melting points (91—92° and 114° respectively) and dissociation constants (0.00886 and 0.00760 respectively) of which showed that they were undoubtedly propyl- and isopropyl-succinic acids respectively.\* Analyses of the acids, I, m. p. 91—92°; II, m. p. 114°, were made.

I. 0.1324 gave 0.2556  $\text{CO}_2$  and 0.0918  $\text{H}_2\text{O}$ . C=52.50; H=7.50.

II. 0.1363 „ 0.2622  $\text{CO}_2$  „ 0.0943  $\text{H}_2\text{O}$ . C=52.45; H=7.68.

$\text{C}_7\text{H}_{12}\text{O}_4$  requires C=52.50; H=7.50 per cent.

The anilic acids of these propyl- and isopropyl-succinic acids, which so far as we know have not yet been described, melt at 148° and 139° respectively.

*B. Propylation (Isopropylation) of Ethyl  $\beta$ -Propylcyanosuccinate and  $\beta$ -Isopropylcyanosuccinate.*

These operations were effected by heating molecular proportions of the sodium derivative of the cyano-compound and the alkyl iodide in solution on the water-bath until the liquid became neutral.

\* Propylsuccinic acid, m. p. 91° (Waltz, *Annalen*, 1882, 214, 59),  $K=0.00886$  (Walden); isopropylsuccinic acid, m. p. 113° (Hlasiwetz and Grabouski, *Annalen*, 1867, 224, 207),  $K=0.0076$  (Walden).

The time required varied from 36 to 48 hours. The liquid was then in each case poured into water and the oils extracted with ether and isolated in the usual manner. Each product was then carefully fractionated and refractionated under reduced pressure, the fractions of lower boiling point, which consisted of a mixture of unchanged cyano-compound and alkyl iodide, were again treated with sodium (in alcohol) and an additional quantity of the iodide. Calculated from the theoretical, the yields of refractionated propylated (isopropylated) products were as follows:

Ethyl $\alpha\beta$ -dipropylcyanosuccinate (from ethyl $\beta$ -propylcyanosuccinate and propyl iodide)	78 per cent.
Ethyl $\alpha\beta$ -diisopropylcyanosuccinate (from ethyl $\beta$ -isopropylcyanosuccinate and isopropyl iodide)	70 "
Ethyl $\alpha$ -propyl- $\beta$ -isopropylcyanosuccinate (from ethyl $\beta$ -isopropylcyanosuccinate and propyl iodide)	81.5 "

These substances are colourless oils, and the following table shows their properties:

	B. p. 19—21 mm.	$d_4^{20}$	$\mu_{Na}$
Ethyl $\alpha\beta$ -dipropylcyanosuccinate.....	176—178°	1.0247	1.4440
Ethyl $\alpha\beta$ -diisopropylcyanosuccinate .....	173—175°	1.0575	1.4492
Ethyl $\alpha$ -propyl- $\beta$ -isopropylcyanosuccinate	175—177°	1.0325	1.4452

On analysing them, the following numbers were obtained:

*Ethyl  $\alpha\beta$ -Dipropylcyanosuccinate.*

0.1996 gave 0.4640  $\text{CO}_2$  and 0.1601  $\text{I}_2\text{O}$ . C = 63.39; H = 8.91.

0.1943 ,, 8.4 c.c. nitrogen at 8° and 772 mm. N = 5.3.

*Ethyl  $\alpha\beta$ -Diisopropylcyanosuccinate.*

0.1930 gave 0.4461  $\text{CO}_2$  and 0.1560  $\text{H}_2\text{O}$ . C = 63.06; H = 8.97.

0.2426 ,, 0.5632  $\text{CO}_2$  ,, 0.1900  $\text{H}_2\text{O}$ . C = 63.26; H = 8.70.

0.1617 ,, 6.4 c.c. nitrogen at 6° and 752 mm. N = 4.99.

*Ethyl  $\alpha$ -Propyl- $\beta$ -isopropylcyanosuccinate.*

0.1720 gave 0.3980  $\text{CO}_2$  and 0.1385  $\text{H}_2\text{O}$ . C = 63.4; H = 8.95.

0.1766 ,, 5 c.c. nitrogen at 10° and 761 mm. N = 5.10.

$\text{C}_{15}\text{H}_{25}\text{O}_4\text{N}$  requires C = 63.6; H = 8.89; N = 4.94 per cent.

### C. Hydrolysis of the Oils.

We experienced some difficulty in devising a good method for hydrolysing the oils we have described in the preceding section. In our earlier experiments, which were all carried out with ethyl  $\alpha\beta$ -diisopropylcyanosuccinate, we tried the effect of boiling the oil with

concentrated hydrochloric acid, a process which we had shown to be admirably adapted to the hydrolysis of the ethyl esters of methyl-substituted cyanosuccinates (Trans., 1899, 75, 855). We found, however, that the diisopropyl compound strongly resisted the hydrolytic action of the acid, and that after 120 hours continuous heating nearly one-third of the oil remained undecomposed. No better result was obtained by heating the oil with the acid, under pressure, at  $150^{\circ}$  for 2 days. An examination of the acid liquor remaining after the removal of any unchanged oil, showed that, besides *cis*- and *trans*- $\alpha$ -diisopropylsuccinic acids, it contained a fair quantity of an acid of the formula  $C_7H_{10}O_4$ , which melted at  $114^{\circ}$ , and subsequently proved to be *mono*-isopropylsuccinic acid. Since analyses of the original oil left no doubt in our minds that it was a pure specimen of ethyl  $\alpha\beta$ -diisopropylcyanosuccinate, and since the *same* oil, when hydrolysed by the following method, yielded no acid other than the two  $\alpha$ -diisopropylsuccinic acids, we can only account for the presence of *mono*-isopropylsuccinic acid among the hydrolytic products when hydrochloric acid was employed, on the supposition that a portion of the oil had lost an isopropyl group during the process.

Experiments with hydrochloric acid having proved unsuccessful, we next proceeded to try several other energetic hydrolytic agents, but found that no one of them singly sufficed to effect the purpose in view; we finally adopted the plan of hydrolysing the oils in two stages, namely, first with alcoholic potash, and then with 50 per cent. sulphuric acid. The process was conducted somewhat as follows.

Twenty grams of the oil were boiled with an alcoholic solution of 16 grams of potassium hydroxide in a reflux apparatus for 36 hours. The oil quickly disappeared, and in a short time a quantity of potassium salt separated. The liquid was subsequently evaporated to dryness on the water-bath in order to expel alcohol, and the residue dissolved in water. The solution was added to a large excess of hydrochloric acid, the whole at once extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate. On distilling off the ether, about 13 grams of an oily acid remained. In the case of the dipropylcyano-compound, this oil soon solidified, and the dipropylcyano-succinic acid was obtained without difficulty in a pure condition.\* In the other two cases, the oils showed no signs of crystallisation, even on prolonged standing in a vacuum over sulphuric acid, and we therefore made no attempt to isolate the cyano-acids. As little, if any, evolu-

\* *Dipropylcyano-succinic Acid*.—A white solid which after recrystallisation from benzene melted at  $192^{\circ}$ . On analysis:

0.2333 g. gave 0.4233  $CO_2$  and 0.1381  $H_2O$ .  $C=58.5$ .  $H=7.78$ .

0.1500 g. gave 0.2444 c.c. nitrogen at  $15^{\circ}$  and 762 mm.  $N=6.26$ .

$C_7H_{10}O_4$  requires  $C=58.15$ ;  $H=7.5$ ;  $N=6.16$  per cent.



tion of ammonia was observed during the process just described, and as the resulting oils contained much nitrogen, the cyano-group must have been practically unacted on by the alcoholic potash.

The oil, or solid cyano-acid, was then dissolved in an excess of 50 per cent. sulphuric acid, and the solution boiled in a reflux apparatus on the sand-bath for 6 hours. During the process, the liquid darkened in colour, and oily particles of the anhydride of the *cis*-succinic acid separated, forming a layer on the surface, and finally, on cooling, crystals were deposited.

### C. Separation of the *cis*- and *trans*-Acids by Distillation with Steam.

The acid liquid just described was at once subjected to distillation with steam, when the oily anhydride of the *cis*-succinic acid was passed over, leaving the *trans*-acid behind. The separation was complete in the cases of *s*-dipropylsuccinic and  $\alpha\alpha_1$ -propylisopropylsuccinic acids, but in the case of *s*-diisopropylsuccinic acid we were never able to distil over the whole of the *cis*-acid as anhydride, and it was necessary to treat the residual *trans*-acid with warm benzene in order to remove last traces of the *cis*-isomeride.

(a) *Distillates*.—These were always turbid with oily particles, and had a strong acid reaction; the oil at once dissolved when the liquid was made alkaline with ammonia. The solution of the ammonium salt was in each case concentrated to a small bulk on the water-bath, strong ammonia being added at intervals in order to counteract any tendency to dissociation. The whole was then added to an excess of strong hydrochloric acid, and the liquid thoroughly extracted with ether. The whole of the *cis*-acid could in this way be obtained in a pure condition.

(b) *Residual Liquors*.—These were thoroughly extracted with ether, whereby the non-volatile *trans*-acids were isolated; these were always obtained in a pure state after one or two recrystallisations from hot benzene, in which the *cis*-acids are very soluble.

### E. General Properties of the Acids.

Anhydrides, anilic acids, and characteristic sparingly soluble calcium salts of the *s*-dipropyl-, *s*-diisopropyl-, and  $\alpha\alpha_1$ -propylisopropylsuccinic acids were obtained by methods similar to those explained in our earlier paper (*loc. cit.*, 859). The following general statements may be made with regard to the properties of the acids.

*Solubility*.—The acids are all sparingly soluble in water, but readily dissolve in alcohol, acetone, and ethyl acetate. The *cis*-acids readily

dissolve in warm benzene, whereas the *trans*-isomerides are either quite insoluble or only very sparingly soluble in that solvent. In the case of the diisopropyl acids, a complete separation of the isomerides can be effected by treatment with warm benzene. No general statement can be made with regard to solubility in chloroform.

*Salts*.—Those of the heavy metals and alkaline earths are sparingly soluble; others are soluble.

*Anhydrides*.—Each acid dissolves in acetyl chloride, forming *its own* anhydride; the *trans*-acids require a much longer treatment, however, than the *cis*-isomerides. The anhydrides are all remarkably stable substances, and can be boiled for a long time with water without undergoing any appreciable change; with aniline, they at once yield characteristic anilic acids. The *trans*-anhydrides are quantitatively converted into *cis*-isomerides on being heated for several hours with acetic anhydride at 170° in sealed tubes.

#### F. *s*-Diisopropylsuccinic Acids.

*trans-s*-Diisopropylsuccinic acid is quite insoluble in hot benzene and melts at 226—228°. On analysis:

0.1057 gave 0.2295 CO<sub>2</sub> and 0.0839 H<sub>2</sub>O. C = 59.22; H = 8.91.

C<sub>10</sub>H<sub>18</sub>O<sub>4</sub> requires C = 59.40; H = 8.91 per cent.

*Silver Salt*.

0.2736, on ignition, gave 0.1412 Ag. Ag = 51.61.

C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>Ag<sub>2</sub> requires Ag = 51.92 per cent.

*Calcium Salt*, C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>Ca.H<sub>2</sub>O.—A specimen, dried over sulphuric acid in a vacuum, on analysis, gave the following results:

0.4248 lost 0.0551 H<sub>2</sub>O at 150°. H<sub>2</sub>O = 12.98.

0.3697 anhydrous salt gave 0.0870 CaO. CaO = 23.53.

Calculated, H<sub>2</sub>O = 13.05; CaO (in anhydrous salt) = 23.33 per cent.

*Anhydride*.—The acid was very slowly acted on by boiling acetyl chloride, upwards of 3 hours being required for its complete solution. The resulting anhydride is a colourless liquid, which, under 752 mm. pressure, distilled over at 263—265°; no signs of crystallisation were evident, even after the substance had stood for many days at 0° over sulphuric acid. On analysis:

0.1533 gave 0.3651 CO<sub>2</sub> and 0.1205 H<sub>2</sub>O. C = 64.95; H = 8.73.

C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> requires C = 65.21; H = 8.69 per cent.

The liquid was not appreciably changed by the prolonged action of boiling water, but it instantly dissolved in a warm 50 per cent. solution of sodium hydroxide. On acidifying the solution, a white, crystal-

line acid was precipitated which melted between  $210^{\circ}$  and  $215^{\circ}$ ; on treating this with hot benzene, a very small quantity of the *cis*-acid (m. p.  $170^{\circ}$ ) was extracted, and the insoluble residue now melted at  $226^{\circ}$ .

It is evident, therefore, that the *trans*-acid, with acetyl chloride, yielded *its own* anhydride, a small portion of which, most probably on distillation, had been converted into the *cis*-modification.

*Anilic acid*, made from a portion of anhydride which had not been distilled, and recrystallised from hot benzene, melted at  $201$ — $202^{\circ}$ . On analysis, it yielded the following results:

0.1719 gave 0.4333  $\text{CO}_2$  and 0.1372  $\text{H}_2\text{O}$ . C = 69.62; H = 8.87.

0.2536 „ 11.33 c.c. nitrogen at  $18^{\circ}$  and 762 mm. N = 5.16.

$\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$  requires C = 69.31; H = 8.66; N = 5.05 per cent.

*Cis-s-Diisopropylsuccinic acid*, recrystallised from hot benzene, melted at  $168$ — $170^{\circ}$ , but after being transformed into the anhydride and reconverted into acid, melted very sharply at  $171^{\circ}$ . On analysis:

0.1520 gave 0.3316  $\text{CO}_2$  and 0.1250  $\text{H}_2\text{O}$ . C = 59.50; H = 9.14.

$\text{C}_{10}\text{H}_{18}\text{O}_4$  requires C = 59.40; H = 8.91 per cent.

*Silver Salt*:

0.1160, on ignition, gave 0.0602 Ag. Ag = 51.89.

$\text{C}_{10}\text{H}_{16}\text{O}_4\text{Ag}_2$  requires Ag = 51.92 per cent.

*Calcium Salt*,  $\text{C}_{10}\text{H}_{15}\text{O}_4\text{Ca}, 4\text{H}_2\text{O}$ .—A specimen dried over sulphuric acid in a vacuum was analysed:

0.3937 lost 0.0927  $\text{H}_2\text{O}$  at  $150^{\circ}$ .  $\text{H}_2\text{O}$  = 23.54.

0.3010 anhydrous salt gave 0.0698 CaO. CaO = 23.19.

Calculated,  $\text{H}_2\text{O}$  = 23.08, CaO (in anhydrous salt) = 23.33 per cent.

It may be here noted that the calcium salt of the acid melting at  $168$ — $169^{\circ}$ , described by Hell and Mayer (*loc. cit.*), had the composition  $\text{C}_{10}\text{H}_{16}\text{O}_4\text{Ca}, 4\text{H}_2\text{O}$ , a circumstance which indicates that their acid was identical with our *cis*-acid.

*Anhydride*.—The acid dissolved very readily in cold acetyl chloride with evolution of hydrogen chloride. The anhydride distilled over between  $250^{\circ}$  and  $260^{\circ}$  under 752 mm. pressure as a colourless liquid which did not solidify even after long standing in a vacuum over sulphuric acid. On analysis:

0.1200 gave 0.2862  $\text{CO}_2$  and 0.0980  $\text{H}_2\text{O}$ . C = 65.16; H = 8.80.

$\text{C}_{10}\text{H}_{16}\text{O}_3$  requires C = 65.21; H = 8.69 per cent.

Like the anhydride of the *trans*-acid, this liquid was remarkably stable, and was not decomposed by boiling water. It dissolved in warm

50 per cent. sodium hydroxide solution, and on acidifying with hydrochloric acid the original acid (m. p.  $171^{\circ}$ ) was precipitated.

*Anilic acid*, prepared from the anhydride and recrystallised from hot benzene, melted at  $184-185^{\circ}$ . On analysis:

0.1521 gave 0.3853  $\text{CO}_2$  and 0.1218  $\text{H}_2\text{O}$ . C = 69.09; H = 8.90.

0.3039 ,, 13.6 c.c. nitrogen at  $17^{\circ}$  and 760 mm. N = 5.21.

$\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$  requires C = 69.13; H = 8.66; N = 5.05 per cent.

*Mutual Conversion of the cis- and trans-Acids.*—(1) *Action of Hydrochloric Acid.*—We have already stated in the introductory portion of this paper that Auwers was unable to effect the slightest change in his acid by heating it in sealed tubes with hydrochloric acid to  $180-200^{\circ}$ . We had a similar experience in the case of the *cis*-acid, but on repeating the experiment at a temperature of  $220-230^{\circ}$  a small but quite appreciable quantity of it was converted into the *trans*-modification. On subjecting the *trans*-acid to the same treatment, by far the greater part was converted into the *cis*-form. The state of equilibrium between the two isomerides finally attained in each of the two experiments was as nearly as possible the same.

(2) *Action of Acetic Anhydride.*—On boiling the *trans*-acid or its anhydride with acetic anhydride, it was gradually converted into the *cis*-anhydride. The conversion was complete in a few hours when the experiment was carried out at  $170^{\circ}$  in sealed tubes.

#### G. *s*-Dipropylsuccinic Acids.

*trans-s-Dipropylsuccinic acid* is slightly soluble in benzene, and completely so in chloroform. It is best recrystallised from a mixture of benzene and light petroleum, and when pure melts at  $182-183^{\circ}$ . On analysis:

0.1628 gave 0.3537  $\text{CO}_2$  and 0.1320  $\text{H}_2\text{O}$ . C = 59.27; H = 9.01.

$\text{C}_{10}\text{H}_{18}\text{O}_4$  requires C = 59.40; H = 8.91 per cent.

#### Silver Salt.

0.2212, on ignition, gave 0.1146 Ag. Ag = 51.84.

$\text{C}_{10}\text{H}_{16}\text{O}_4\text{Ag}_2$  requires Ag = 51.92 per cent.

*Calcium Salt*,  $\text{C}_{10}\text{H}_{16}\text{O}_4\text{Ca}, 2\text{H}_2\text{O}$ .—Specimen dried in a vacuum over sulphuric acid. On analysis:

0.1922 lost 0.0259  $\text{H}_2\text{O}$  at  $150^{\circ}$ .  $\text{H}_2\text{O}$  = 13.50.

0.1998 of anhydrous salt gave 0.0462 CaO. CaO = 23.13.

Calculated:  $\text{H}_2\text{O}$  = 13.06; CaO (in anhydrous salt) = 23.33 per cent.

*Anhydride.*—The acid dissolved more readily than the *trans*-diisopropyl acid in boiling acetyl chloride, only 45 minutes being required

for complete solution. The anhydride is a colourless liquid, which distilled over at 269—274° under 768 mm. pressure. On analysis :

0.1721 gave 0.4101 CO<sub>2</sub> and 0.1349 H<sub>2</sub>O. C=65.00 ; H=8.71.

C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> requires C=65.21 ; H=8.69 per cent.

A portion of the liquid was dissolved in a hot 50 per cent. solution of sodium hydroxide, and on acidifying the solution with hydrochloric acid, an acid melting at 160—170° separated, from which a small quantity of the *cis*-acid (m. p. 115—117°) could be extracted with benzene.

It is evident therefore that, as in the case of the *s*-diisopropyl acids, some of the *trans*-anhydride was, on distillation, converted into the *cis*-modification, for the undistilled anhydride yielded only the sodium salt of the *trans*-acid on being dissolved in sodium hydroxide.

*Anilic acid*, prepared from undistilled anhydride and recrystallised from benzene, melted at 184—185°. On analysis :

0.1121 gave 0.2831 CO<sub>2</sub> and 0.0902 H<sub>2</sub>O. C=68.90 ; H=8.94.

0.2444 „ 10.9 c.c. nitrogen at 18° and 764 mm. N=5.20.

C<sub>16</sub>H<sub>23</sub>O<sub>3</sub>N requires C=69.31 ; H=8.66 ; N=5.05 per cent.

*cis-s-Dipropylsuccinic acid*, when recrystallised from benzene, melted at 115—117°, but on being transformed into anhydride and then reconverted into acid, melted at 119—121°. On analysis :

0.1698 gave 0.3690 CO<sub>2</sub> and 0.1347 H<sub>2</sub>O. C=59.26 ; H=8.99.

C<sub>10</sub>H<sub>16</sub>O<sub>4</sub> requires C=59.40 ; H=8.91 per cent.

*Silver Salt*.

0.2364, on ignition, gave 0.1224 Ag. Ag=51.79.

C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>Ag<sub>2</sub> requires Ag=51.92 per cent.

*Calcium Salt*, C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>Ca.H<sub>2</sub>O.—Specimen dried in a vacuum over sulphuric acid. On analysis :

0.3127 lost 0.0225 H<sub>2</sub>O at 150°, H<sub>2</sub>O=7.20.

0.4390 anhydrous salt gave 0.1021 CaO. CaO=23.26.

Calculated : H<sub>2</sub>O=6.96 ; CaO (in anhydrous salt)=23.33 per cent.

*Anhydride*.—The acid dissolved very rapidly in cold acetyl chloride. The resulting anhydride was a colourless liquid which distilled at 266—270° under 768 mm. pressure. On analysis :

0.1433 gave 0.3421 CO<sub>2</sub> and 0.1134 H<sub>2</sub>O. C=65.10 ; H=8.80.

C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> requires C=65.21 ; H=8.69 per cent.

The liquid was dissolved in a hot 50 per cent. solution of sodium hydroxide; on acidifying the solution with hydrochloric acid, the original *cis*-acid, melting at 119—121°, was precipitated.

*Anilic acid*, prepared from the anhydride, and recrystallised from benzene, melted at 101—102°. On analysis:

0.1441 gave 0.3672 CO<sub>2</sub> and 0.1098 H<sub>2</sub>O. C=69.48; H=8.47.

0.2649 gave 12 c.c. nitrogen at 18° and 764 mm. N=5.26.

C<sub>16</sub>H<sub>23</sub>O<sub>3</sub>N requires C=69.31; H=8.66; N=5.05 per cent.

*Mutual Conversion of the cis- and trans-Acids.* (1) *Action of Hydrochloric Acid*.—When either isomeride was heated with strong hydrochloric acid for 10 hours at 180° in sealed tubes, a mixture of the two, containing about 95 per cent. of the *trans*-acid, was obtained. These results form a striking contrast with the corresponding experiments on the *s*-diisopropyl acids, where it was shown that the *cis*-acid was not changed in the slightest degree by the action of hydrochloric acid at 180°, and is only to a very small extent converted into the *trans*-form at 220—230°.

(2) *Action of Acetic Anhydride*.—The *trans*-acid (or anhydride) is completely converted into the *cis*-anhydride by being heated for 5 hours in sealed tubes with acetic anhydride.

#### H. $\alpha\alpha_1$ -Propylisopropylsuccinic Acids.

The investigation of these acids, as will be explained later, was undertaken for the express purpose of determining the influence of the 'propylisopropyl' combination upon the electrical conductivities of two stereoisomeric 'succinic' acids.

*trans- $\alpha\alpha_1$ -Propylisopropylsuccinic acid* is a beautiful, crystalline powder, which, after recrystallisation from a mixture of benzene and light petroleum, melts at 192—194°. On analysis:

0.1861 gave 0.4048 CO<sub>2</sub> and 0.1529 H<sub>2</sub>O. C=59.33; H=9.13.

C<sub>10</sub>H<sub>18</sub>O<sub>4</sub> requires C=59.40; H=8.91 per cent.

##### *Silver Salt.*

0.1572 yielded, on ignition, 0.0816 Ag. Ag=52.11.

C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>Ag<sub>2</sub> requires Ag=51.92 per cent.

*Calcium Salt* is anhydrous. On analysis:

0.3104, on ignition, gave 0.0519 CaO. CaO=16.71.

C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>Ca requires CaO=16.66 per cent.

*Anhydride*, prepared as usual. A colourless liquid which distilled at 265—272° under 742 mm. pressure. On analysis:

0.1179 gave 0.2811 CO<sub>2</sub> and 0.0942 H<sub>2</sub>O. C=65.02; H=8.88.

C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> requires C=65.21; H=8.69 per cent.

The oil dissolved in a hot 50 per cent. sodium hydroxide solution, giving the sodium salt of the original *trans*-acid.

*Anilic acid*, prepared from the anhydride and aniline, melted at 147—149° after recrystallisation from dilute alcohol. On analysis:

0.1928 gave 8.75 c.c. nitrogen at 13° and 749 mm.  $N = 5.26$ .

$C_{16}H_{23}O_3N$  requires  $N = 5.05$  per cent.

(b) *cis-s-Propylisopropylsuccinic acid* crystallised in small plates with silvery lustre from a mixture of chloroform and light petroleum. It melted at 151—152°. On analysis:

0.2011 gave 0.4360  $CO_2$  and 0.1631  $H_2O$ .  $C = 59.13$ ;  $H = 8.91$ .

$C_{10}H_{18}O_4$  requires  $C = 59.40$ ;  $H = 8.91$  per cent.

*Silver Salt*.

0.1552, on ignition, gave 0.0807 Ag.  $Ag = 52.00$ .

$C_{10}H_{16}O_4Ag_2$  requires  $Ag = 51.92$  per cent.

*Calcium Salt*,  $C_{10}H_{16}O_4Ca \cdot 2H_2O$ . On analysis:

0.6221 lost 0.0828  $H_2O$  at 150°.  $H_2O = 13.31$ .

0.3326 anhydrous salt gave 0.0551  $CaO$ .  $CaO = 16.51$ .

Calculated,  $H_2O = 13.04$ ;  $CaO$  (in anhydrous salt) = 16.66 per cent.

*Anhydride*.—A colourless liquid which distilled at 265—275° under 742 mm. pressure. On analysis:

0.1028 gave 0.2449  $CO_2$  and 0.0824  $H_2O$ .  $C = 64.99$ ;  $H = 8.91$ .

$C_{10}H_{16}O_3$  requires  $C = 65.21$ ;  $H = 8.69$  per cent.

The oil dissolved in a hot 50 per cent. solution of sodium hydroxide, yielding the sodium salt of the original *cis*-acid.

*Anilic acid* from anhydride and aniline. This, as distinguished from all anilic acids of substituted succinic acids which we have hitherto examined, is a liquid. All attempts to induce solidification failed.

*Mutual Conversion of the cis- and trans-Acids*. (1) *Action of Hydrochloric Acid*.—On heating either the *cis*- or *trans*-acid in sealed tubes with hydrochloric acid at 200°, about half of it is converted into the isomeric form.

(2) *Action of Acetic Anhydride*.—As in the case of the other acids described in the paper, the *trans*-modification can be quantitatively converted into the *cis*-anhydride by being heated in sealed tubes with acetic anhydride at 150°.

### K. Dissociation Constants of the Acids.

The study of the dissociation constants of the acids we have described in the foregoing sections of this paper has yielded such remarkable results that we feel justified in discussing them separately at some length.

Considering the constants of the 'succinic' series as a whole, it may be pointed out that the replacement of one hydrogen in the molecule of succinic acid by an alkyl radicle is invariably accompanied by an increase in electrical conductivity, and, therefore, of the dissociation constant. Thus :

	100%*.
Succinic acid.....	0.0068
Monomethylsuccinic acid.....	0.0085
Monoethyl     "     " .....	0.0085
Monopropyl   "     " .....	0.00886
Monoisopropyl "     " .....	0.0076

It will also be noted that whereas the 'normal' radicles appear to have much the same influence on the conductivity, an "iso"-grouping raises it to a much smaller extent. The substitution of a second hydrogen by an alkyl radicle may occur in one of two possible ways according as the second alkyl replaces a hydrogen attached to the same or to a different carbon atom as that to which the first alkyl was attached. Only one example of the first-named type of acid, namely, *α*,*α*-dimethylsuccinic acid, has so far been studied from this point of view, and its constant (0.0080) is practically the same as that of the monomethyl acid. On the other hand, quite a number of *s*- or *α*<sub>1</sub>-dialkylsuccinic acids have been investigated, all of which, of course, exist in two stereoisomeric forms. Experience shows that the substitution of the *second* hydrogen by alkyl in such cases invariably increases the dissociation constant to a much greater extent than did the first alkyl substitution increase that of succinic acid, and, further, that two stereoisomerides in each case generally have nearly the same constants. Thus :

	<i>trans</i> -Acid.	<i>cis</i> -Acid.
<i>s</i> -Dimethylsuccinic.....	0.0196	0.0123
<i>s</i> -Diethylsuccinic.....	0.0245	0.0201
<i>α</i> <sub>1</sub> -Methylethylsuccinic .....	0.0207	0.0201
<i>α</i> <sub>1</sub> -Methylallylsuccinic .....	0.0243	0.0233
<i>α</i> <sub>1</sub> -Ethylallylsuccinic .....	0.0269	0.0359

In the case of tri- or tetra-substituted acids, our present knowledge is limited to the methyl compounds; the constants of these, however (trimethyl- = 0.032 and tetramethyl- = 0.033), show still the tendency of successive alkyl substitutions to increase the conductivities in the series.

On determining the constants of our *s*-diisopropyl acids we were astonished to find, not only that that of the *cis*-acid was very much

\* The values for 100% quoted in this and following table are those which appear to be the most probable according to determinations made by Walden, Walker, ourselves, and others.



greater than that of any other previously known member of the series, but also that it was over *twenty* times as great as that of the isomeric *trans*-acid. The actual numbers obtained were :

*trans*-s-Diisopropylsuccinic Acid (temp. 25°).

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
256	53.7	0.1535	0.01081
512	73.15	0.2090	0.01088
1024	98.86	0.2824	0.01077
2048	129.7	0.3691	0.01057

$$K = 0.0108.$$

*cis*-s-Diisopropylsuccinic Acid (temp. 25°).

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
128	146.8	0.4191	0.2368
256	183.6	0.5246	0.2262
512	233.8	0.6395	0.2209
1024	262.4	0.7491	0.2183

$$K = 0.2300.$$

In the first place, it will be observed that the value of *k* for our *cis*-acid approximates to that given by Auwers for the acid he obtained from ethyl  $\alpha$ -bromoisovalerate (0.2938), but that, whereas his values diminished considerably on dilution (see p. 655), ours remain nearly constant. The chemical properties of the two acids (his and ours) are so much alike that we are not disposed to doubt their identity. But since the *trans*-acid is now shown to have a constant less than one-twentieth that of the *cis*-isomeride, Auwers' conductivity results can hardly be explained on the supposition that he was dealing with a mixture of the two in which the *cis*-form predominated. As a matter of fact, we made a mixture of 9 parts of the *cis*-acid with 1 part of the *trans*-acid, and although the mixture melted in the neighbourhood of 178° (the temperature given by Auwers as the melting point of his acid), its "dissociation constant" (if such a term can be strictly applied to a variable quantity) was always much lower than that of the pure *cis*-acid, thus :

*Mixture of 90 per cent. cis- with 10 per cent. trans*-s-Diisopropylsuccinic Acids (temp. 25°).

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
384	152.2	0.4342	0.0869
768	181.1	0.5174	0.0722
1536	211.1	0.6028	0.0596
3072	215.5	0.6157	0.0321

The chief interest, however, connected with these results is the indication they afford that the constants of two stereoisomeric saturated acids may differ very greatly. Professor J. Walker has in a private communication drawn our attention to the fact that the constant for maleic acid ( $k=1.17$ ) is thirteen times as great as that of fumaric acid ( $k=0.093$ ). But the two cases are in no wise parallel, for the stereoisomerism of two *s*-dialkylsuccinic acids is of a totally different character from that of maleic and fumaric acids, although it must be confessed that the conventional use of the terms *trans*- and *cis*- in the case of the former is misleading.

Our experiments on the conductivities of the two *s*-dipropylsuccinic acids yielded the following numbers :

*trans-s-Dipropylsuccinic Acid* (temp. 25°).

$v.$	$\mu_{90}$	$m.$	100%.
256	78.78	0.2250	0.02552
512	106.1	0.3031	0.02380
1024	144.4	0.4126	0.02337
2048	163.6	0.4675	0.02287

$$K=0.025.$$

*cis-s-Dipropylsuccinic Acid* (temp. 25°).

$v.$	$\mu_{90}$	$m.$	100%.
128	77.41	0.2212	0.04908
256	103.91	0.2966	0.04883
512	136.41	0.3893	0.04857
1024	173.5	0.4957	0.04759

$$K=0.049.$$

There is nothing extraordinary about these results, for although there is a marked difference between the constants of the two stereoisomerides, it is not abnormal. Thinking that the exceptional behaviour of the *s*-diisopropyl acids might be connected with the isopropyl grouping, we determined to examine  $\alpha\alpha_1$ -methylisopropyl- and  $\alpha\alpha_1$ -propylisopropyl-succinic acids. Professor Perkin was kind enough to furnish us with specimens of the two inactive isomerides of the former,\* whilst those of the latter were of our own preparation. Conductivity determinations gave the following results :

\* The  $\alpha\alpha_1$ -methylisopropylsuccinic acids were described in a paper by W. H. Bentley, W. H. Perkin, jun., and J. F. Thorpe (Trans., 1896, 69, 270).

*trans- $\alpha\alpha_1$ -Methylisopropylsuccinic Acid* (m. p. 174—175°).

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
161.7	51.75	0.1478	0.01543
323.4	70.45	0.2013	0.01570
646.8	95.75	0.2735	0.01590
1293.6	127.1	0.3633	0.01602

$$K = 0.0158.$$

*cis- $\alpha\alpha_1$ -Methylisopropylsuccinic Acid* (m. p. 125—126°).

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
90.8	75.35	0.2154	0.0652
181.6	101.98	0.2913	0.0659
363.2	135.2	0.3862	0.0669
726.4	173.8	0.4957	0.0671

$$K = 0.066.$$

*trans- $\alpha\alpha_1$ -Propylisopropylsuccinic Acid* (temp. 25°).

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
256	61.74	0.1764	0.0149
512	82.85	0.2367	0.0144
1024	112.7	0.3219	0.0147
2048	143.6	0.4103	0.0139

$$K = 0.0147.$$

*cis- $\alpha\alpha_1$ -Propylisopropylsuccinic Acid* (temp. 25°).

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
128	62.63	0.1790	0.0297
256	83.90	0.2397	0.0295
512	104.5	0.3200	0.0294
1024	145.4	0.4164	0.0290

$$K = 0.0295.$$

Thus, we find in the case of the  $\alpha\alpha_1$ -methylisopropyl acids that the constant of the *cis*- is four times that of the *trans*-isomeride, whereas there is no greater difference between the two stereoisomeric  $\alpha\alpha_1$ -propylisopropyl acids than there is between the corresponding two *s*-dipropyl acids. Hence it would seem that the peculiar behaviour of the two diisopropyl acids is in some measure due to the additive effect of the two isopropyl groups. In order to see whether this was wholly so or not, we prepared and determined the constants of the methyl hydrogen salts of the two *s*-diisopropyl acids. We were astonished to find that the masking of one of the carboxyl groups, whilst it only lowered the

constant of the *trans*-acid by about 40 per cent., reduced that of the *cis*-acid to one-twentieth of its original value. Thus :

*Methyl Hydrogen trans-s-Diisopropylsuccinate.*

<i>v.</i>	$\mu_{\nu}$	<i>m.</i>	100 <i>k.</i>
380	50.37	0.1439	0.00636
760	68.64	0.1961	0.00629
1520	91.40	0.2611	0.00616
3040	118.1	0.3453	0.00599

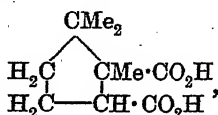
$$K = 0.0063.$$

*Methyl Hydrogen cis-s-Diisopropylsuccinate.*

<i>v.</i>	$\mu_{\nu}$	<i>m.</i>	100 <i>k.</i>
238	52.87	0.1510	0.01129
476	73.08	0.2087	0.01153
952	98.26	0.2807	0.01153
1904	130.6	0.3731	0.01166

$$K = 0.0115.$$

The foregoing results, which for the sake of reference we have tabulated at the end of this paper, indicate that the connection between the dissociation constant and constitution of an organic acid is not so direct as many would have us believe it to be. Professor Walker has recently stated (*Trans.*, 1900, 77, 398) that the increase in the constant of succinic (or glutaric) acid when the hydrogens are successively replaced by alkyl groups, is not due to the primary effect of the substitution, but rather to an increase in the proximity of the two carboxyl groups. Adopting the Perkin-Bouveault formula for camphoric acid, which represents it as a succinic derivative, as follows :



he accounts for its small dissociation constant (0.0025) by saying that the rigidity of the ring formation prevents the approximation of the carboxyl radicles, and thus allows the primary effect of substitution to become manifest. The view that the proximity of the carboxyl radicles in succinic acid increases as the hydrogen is successively replaced by alkyl groups, is supported by the fact that the tendency to anhydride formation is more marked as the number of alkyl-substituted groups increases, but our results show that such considerations do not wholly explain the facts. Since our experience is that *cis-s*-di-

propylsuccinic acid yields an anhydride with acetyl chloride if anything more readily than does the *cis*- $\alpha$ -diisopropyl acid, it can hardly be contended that the two carboxyl radicles in the latter are nearer each other than they are in the former, and yet the constant of the latter is nearly five times as great as that of the former. We hope shortly to publish, in conjunction with Dr. Sudborough, important evidence on these matters derived from a study of the methyl hydrogen salts of substituted succinic acids, but the facts recorded in our present communication are sufficient to show that the subject calls for much further investigation before any general principle can legitimately be deduced.

*Table of Dissociation Constants.*

Acid.	<i>Trans.</i>	<i>Cis.</i>	Approx. ratio.
<i>s</i> -Dipropylsuccinic .....	0·025	0·049	1 : 2
$\alpha\alpha$ -Propylisopropylsuccinic .....	0·0147	0·0295	1 : 2
$\alpha\alpha$ -Methylisopropylsuccinic.....	0·0158	0·066	1 : 4
<i>s</i> -Diisopropylsuccinic .....	0·0108	0·2300	1 : 20
Methyl hydrogen <i>s</i> -diisopropylsuccinate .....	0·0063	0·0115	1 : 2

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## LVI.—*The Interaction between Sulphites and Nitrites.*

By EDWARD DIVERS and TAMEMASA HAGA.

THE present paper gives an account of a series of experiments the results of which seem to leave no room for doubt as to the truth of the following propositions respecting the sulphonation of nitrites : (1) normal sulphites have no action on nitrites ; (2) pyrosulphites react but partially with nitrites ; (3) pyrosulphites react completely with nitrous acid or its equivalent of nitric oxide and nitric peroxide (nitrous fumes) ; and (4) sulphurous acid and nitrous acid, or the oxides and water equivalent to them, interact in such a way that the base of the sulphite, that may be used in place of the sulphurous acid, is needed only to preserve from hydrolysis the products of the interaction. Concerning these assertions, we would point out that

the *first* directly contradicts the conclusions drawn by other workers from their experiments; the *second* is novel like the first, the facts on which it is based having been hitherto misunderstood; the *third* has been enunciated before but only on theoretical grounds; lastly, the *fourth* has also been made before, but upon a basis of experimental evidence quite inadequate to justify it.

The establishment of these propositions, taken along with what we have already published as to the constitution of Fremy's salts, will then allow of the further assertion being made that the interaction of nitrous acid with a pyrosulphite results in the formation of a two-thirds normal hydroximidodisulphate, the other sulphazotised salts being secondary products derived from it. It is thus established that the only interaction between sulphites and nitrites is one of the greatest simplicity, instead of being full of complications, as hitherto believed.

*Ia. A Normal Sulphite has no Action on a Nitrite.*

Dipotassium or disodium sulphite has no action on a nitrite. In establishing this fact, we have left mixed solutions of normal sulphite and nitrite in varying proportions in closely corked flasks for days and for weeks, but no change has ever occurred; for, when coloured with rosolic acid, a drop of dilute acid would at any time, as at first, discharge the colour. Had any action occurred, alkali hydroxide must have been generated (as to the possibility of which, see sect. IIb). A portion of the solution, to which a drop of dilute sulphuric acid had been added, re-acquired the pink colour of the rosolic acid when left for some time, the minute quantity of pyrosulphite which the acid had liberated having slowly interacted with the nitrite, but when that was used up, no more action occurred, and, at any time, one drop of dilute acid would again remove the colour of the solution.

Further proof of this inactivity is afforded by the fact that, whilst potassium pyrosulphite with a nitrite gives rise to the insoluble nitrilosulphate, no separation of this salt occurred in the above experiments. Again, barium chloride, added to the alkaline mixture of normal sulphite with nitrite, threw down all the sulphur as sulphite, and left the nitrite in solution neutral to litmus. Had sulphazotised salts been present, precipitation of the sulphur would have been incomplete, and the mother liquor would have remained strongly alkaline to litmus, and when acidified would have deposited barium sulphate quickly in the cold and at once if boiled.

Fremy, Claus, and Raschig all believed that dipotassium sulphite acted on potassium nitrite, although the last named chemist recognised the value also of the pyrosulphite, as Berglund had done before him.

Fremy apparently used sulphite neutral to litmus and took it to be the normal salt, and Claus certainly did so. Since, therefore, they used sulphite which was, for the most part, pyrosulphite, no evidence on the point in question can be gathered from their work. We would account for Fremy's finding that sodium sulphite had no action on sodium nitrite, otherwise inexplicable, by assuming that the solution of sodium sulphite which he used happened to contain no pyrosulphite. Claus's statement that some potassium sulphite neutral to litmus acted as strongly on nitrite, after he had added potash 'in excess' to it, as it did before, is explicable if we assume that the excess spoken of was large enough to give the solution a markedly alkaline action on litmus and yet small enough to leave much pyrosulphite unchanged.

*Ib. Potassium Hydroxide not a Factor in the Formation of the Sulphazotised Salts.*

That normal potassium or sodium sulphite remains without action on a nitrite when alkali hydroxide is added was ascertained by leaving the three substances together in solution in a closed flask for some time, as in the preceding section, and then precipitating with barium chloride after the addition of ammonium chloride; no sulphur compound was left in the filtrate. [Ammonium chloride prevents precipitation of hydroximidosulphate (Trans., 1894, 65, 545, 559)].

On the many occasions we have had to prepare sulphazotised potassium salts by submitting solutions of nitrite and hydroxide to the action of sulphur dioxide, taking care to keep the solution briskly agitated, we have found that, even in ice-cold solutions, precipitation of these very sparingly soluble salts only begins from the point at which there is no more hydroxide left, and then goes on freely until the solution has become neutral to lacmoid paper. In proportion as the hydroxide disappears, sulphite becomes abundant, whilst from the time that the replacement of hydroxide by sulphite is complete, the quantity of sulphite steadily decreases as the sulphazotised salts form. Sulphazotised sodium salts being very soluble, no precipitation occurs during their preparation, and with these, therefore, we made an experiment to determine quantitatively what happens up to the point when the last portion of hydroxide disappears, as indicated by rosolic acid losing its pink colour.

Washed sulphur dioxide was sent in a steady stream into a solution of 11.21 grams NaHO and 19.34 grams sodium nitrite in 198 c.c. of water, kept in active motion and immersed in ice. The sodium compounds were in molecular proportion, but excess of nitrite would not have mattered. In a short time, 10 c.c. were removed by a pipette;

soon after a second quantity, and not very long after a third, just as the pink colour of the rosolic acid had disappeared. The three portions were treated alike. Each was mixed with excess of solutions of ammonium and barium chlorides and the precipitate filtered off, oxidised to sulphate, washed with dilute hydrochloric acid, and weighed as barium sulphate. By evaporating the ammonium chloride filtrate to dryness, all the sulphur of the sulphazotised salts was converted into sulphate by the nitrite and ammonium chloride. The soluble salts were washed out with dilute hydrochloric acid, and the barium sulphate collected and weighed. The solution of salts removed from the barium sulphate was concentrated and then heated under pressure for some hours, after which it was found to be still clear and therefore free from sulphate, showing that no sulphazotised salt escaped decomposition during the evaporation.

We give the quantities of sulphur dioxide found in each pipetteful as sulphite and as sulphazotised salts, and also state these quantities as parts per hundred of the total sulphur dioxide which had entered it.

Sulph. diox. as	1st 10 c.c.	2nd 10 c.c.	3rd 10 c.c.
Sulphite ...	0.0662 gram=96.6	0.1204 gram=96.5	0.3996 gram=91.5 per cent.
Sulphazot..	0.0023 „ = 3.4	0.0047 „ = 3.5	0.0365 „ = 8.5 „

It will be seen that all but 3.5 per cent. of the sulphur dioxide entering the solution in the early stages of the experiment remained in the form of sulphite, and that even up to the time when the last of the hydroxide had been consumed, all but 8.5 per cent. of the total sulphur dioxide was in the state of sulphite. That it must be impossible to prevent a temporary local excess of sulphur dioxide will be at once admitted, as also that it must be difficult in the later stages to keep down this local excess to very narrow limits. Therefore it will seem in the highest degree probable, if not certain, from this experiment that sulphur dioxide, equally with normal sulphite, does not act on nitrite in presence of alkali hydroxide.

As Fremy believed that potassium hydroxide helps the formation of sulphazotised salts, he added it occasionally when passing sulphur dioxide into a solution of potassium nitrite, and to such an extent that at the end of the operation the mother liquor of his salts was so strongly alkaline as to be destructive to filter paper. Claus, although he did not believe that the potash exercised any specific influence on the action, agreed with Fremy as to its value in precipitating and preserving the sulphazotised salts, and consequently stopped passing in sulphur dioxide as soon as the alumina contained in the potassium hydroxide began to precipitate, as this occurs while the solution is still strongly alkaline. Raschig, in attempting to prepare Fremy's



*sulphazate*, also used this precipitation of alumina as the indication to stop the process.

From this, it would seem that Fremy, Claus, and Raschig have all prepared sulphazotised salts without difficulty under conditions which we pronounce to be incompatible with their production. This apparent contradiction may be explained by assuming, for one thing, that, in Fremy's way of working, success followed only because, temporarily and locally, the point of saturation of the alkali was reached and exceeded, again and again, where the gas entered the solution, and there is nothing to show that, to check this, he kept his solution well agitated. Secondly, we can assume, with great probability, that his solution often lost its alkalinity between the additions of the hydroxide which he made. Working as we believe he actually did, we have found it easy to get results similar to his. So far as Claus and Raschig followed Fremy's method, their results are equally open to objection, whilst it is to be remarked of their alumina indicator that, not only is normal sulphite strongly alkaline to litmus, but, as we have found, any aluminium present is precipitated as hydroxide just when the sulphur dioxide has converted all alkali into normal sulphite. They will, therefore, in their experiments, have preserved none of the alkali unchanged and most probably have generated also some pyrosulphite. There is, besides, indirect evidence in Claus's work that normal sulphite is either inactive or acts only very slowly on nitrite, for when, having taken no excess of this salt, he stopped the process just after precipitation of alumina, much of this nitrite remained in the solution, and, as we have just pointed out, much normal sulphite must also have been present. The two salts were, therefore, together in solution unchanged. Raschig, too, found that sulphite and nitrite do not act on each other when in presence of potassium hydroxide dissolved in its own weight of water.

*IIa. Even a Pyrosulphite is only active on a Nitrite until it has become Normal Sulphite.*

Pyrosulphite, neutral to lacmoid paper and containing, therefore, neither sulphurous acid nor normal sulphite, freely sulphonates nitrite, but is far from being all consumed in the process, as it has been represented to be by Claus, Berglund, and Raschig. Quantitative experiments have shown us that, when pyrosulphite is left in solution with excess of nitrite in a closed vessel for a considerable time, about one-third of the sulphite remains inactive by becoming converted into the normal salt, separable, as in other cases, from the sulphazotised salts by precipitation with barium chloride in presence of ammonium chloride. From this, it follows that 3 mols. of pyro-

sulphite are needed to convert 2 mols of nitrite into hydroximidodisulphate (Trans., 1894, 65, 526) and not 2 mols. only, as had been supposed. The third mol. of sulphite remains unavoidably in the solution, but all the nitrite is sulphonated,  $2\text{NaNO}_2 + 3\text{Na}_2\text{S}_2\text{O}_5 + \text{OH}_2 = 2\text{Na}_2\text{HNS}_2\text{O}_7 + 2\text{Na}_2\text{SO}_3$ . Using less pyrosulphite, some nitrite remains at the end along with normal sulphite. That sodium pyrosulphite cannot easily be entirely used up in sulphonating sodium nitrite was observed by Raschig.

Not only is hydroximidodisulphate formed, but a little nitrilosulphate also, when a pyrosulphite acts on a nitrite, but if ordinary care is taken, this need never be enough to cause much less than one-third of the sulphite to remain inactive. If excess of pyrosulphite is used, the interaction appears to be  $\text{NaNO}_2 + 2\text{Na}_2\text{S}_2\text{O}_5 = \text{Na}_2\text{NS}_3\text{O}_9 + \text{Na}_2\text{SO}_3$ , but we have not made any quantitative determination of the sulphite remaining, the qualitative evidence being sufficient.

The interaction between pyrosulphite and nitrite proceeds at first very rapidly and with great elevation of temperature, but when the temperature is kept down by cooling, it is soon retarded, so that many hours are then required for its completion. The normal sulphite seems here to inhibit the action of the pyrosulphite, just as the salt of a weak acid inhibits the action of that acid, an effect now well recognised. This consideration points to the propriety of regarding the passage of pyrosulphite to normal sulphite as its action as an acid on the nitrite, and not as the yielding up of half of its sulphurous acid for the sulphonation of the nitrite, the interactions being  $2\text{NaNO}_2 + \text{Na}_2\text{S}_2\text{O}_5 + \text{OH}_2 = 2\text{HNO}_2 + 2\text{Na}_2\text{SO}_3$ , and then  $2\text{HNO}_2 + 2\text{Na}_2\text{S}_2\text{O}_5 = 2\text{Na}_2\text{HNS}_2\text{O}_7$  (see section IIIa).

#### *Iib. Alkali is not produced in the Sulphonation of a Nitrite.*

One of the most remarkable things, according to Claus, is the production of potassium hydroxide in the formation of Fremy's salts through the agency of a sulphite. He explained this production by the equation  $\text{KNO}_2 + 2\text{K}_2\text{SO}_3 + 2\text{H}_2\text{O} = \text{K}_2\text{HNS}_2\text{O}_7 + 3\text{KHO}$ . Such an equation was also published by Berglund (*Lunds. Univ. Årskr.*, 1875, 13, 14). Raschig gave the same equation for results obtained by himself and, in order to express other results, gave also the equation  $\text{NaNO}_2 + 2\text{NaHSO}_3 = \text{Na}_2\text{HNS}_2\text{O}_7 + \text{NaHO}$ . Finding also, as Claus had done, that dipotassium hydroximidodisulphate does not combine at once or even at all with potassium hydroxide, he argued that this salt cannot have a constitution similar to that of Fremy's 'basic' sulphazotate because potassium hydroxide is produced along with it instead of being combined with it as Fremy's 'basic' sulphazotate.

Now, all this is wrong in fact, both on the part of Claus and of

Raschig, as we have already shown (Trans., 1894, 65, 533), or show in other sections of the present paper, except as to the generation of alkali hydroxide, with which we now proceed to deal. Claus's emphatic statement, supported as it is by Berglund and by Raschig, that potassium hydroxide is formed when a sulphite meets a nitrite in solution, rests upon no other evidence than what we now set down in full, recalling the fact (section Ia) that between the normal sulphite and nitrite there is really no action of any kind. A solution of sulphite made neutral to litmus and a solution of nitrite of either potassium or sodium become hot and strongly alkaline to litmus when mixed together, and then contain much hydroximidosulphate and nitrilosulphate, both neutral to litmus, which soon crystallise out if they are the potassium salts. That is all these chemists had as evidence for the production of the hydroxide; let us add to it the fact that the addition of excess of barium chloride removes all the alkalinity. It follows, since pyrosulphites are a little acid to litmus and normal sulphites are very alkaline to it, that the phenomena depended on offer no grounds whatever for the belief that alkali hydroxide is produced. Except by the use of lime, baryta, or other base, there is, we believe, only one way by which potassium hydroxide can be generated from potassium sulphite, and that is one made known by us, namely, treatment of the sulphite first with nitric oxide and then with alcohol and water (Trans., 1895, 67, 1098).

### IIIa. *A Pyrosulphite reacts completely with Nitrous Acid.*

As remarked at the end of section IIa, a pyrosulphite appears to act as an acid on the nitrite and then sulphonates the nitrous acid itself,—only indirectly, therefore, sulphonating the nitrite of a metal or of ammonium. One-third of the pyrosulphite should, accordingly, be replaceable by some other acid, and so it proves to be (section III d). It is not new to formulate the sulphonation of  $\text{HNO}_2$ , and to speak of 'nitrous acid' as the reacting substance, for (passing over Fremy) Raschig has already done so; but, whilst we would be understood to confine the activity to nitrous acid itself, or its acidic equivalents (section III d), such was not the thought of Raschig, who only wrote H as a general symbol, and 'acid' as a general term, whilst representing metallic nitrites as active by generating alkali hydroxide.

Nor is it new to learn that nitrous acid can be sulphonated. By treating a dissolved sulphite with nitrous acid (nitrous fumes), Fremy did succeed in obtaining sulphazotised salts, but the difficulty of moderating the flow of the gas, and the presence in it of nitrogen peroxide and nitric acid, made the operation so inconvenient, he said, that he did not use it in preparing any of the salts he examined, and

gave no further attention to it. We have taken up the matter, since untouched and unmentioned, where Fremy left it half a century ago. Our work has been very simple but very effective, and has consisted in subjecting a solution of pyrosulphite (and of normal sulphite, but of that we treat in section IIIb) to nitrous fumes which act as nitrogen trioxide when of the right composition. The gases were fully absorbed by a concentrated solution of potassium pyrosulphite kept cold in a flask immersed in ice and brine and well agitated; soon there was an abundant precipitation of hydroximidosulphate mixed with a little nitrilosulphate. While still much pyrosulphite remained unaltered, the process was stopped and the mother liquor at once drained off. In this way, we were very successful in getting much hydroximidosulphate and only a little nitrilosulphate, notwithstanding the presence all along of so much pyrosulphite for, as was pointed out by us long ago, in sufficiently cold solutions sulphonation to nitrilosulphate hardly occurs.

The next five sections (IIIb, c, d, e, f) treat of various mixtures which, from the acid constitution of one of the components, behave like that of nitrite and pyrosulphite, that is, as if each contained pyrosulphite and nitrous acid.

### IIIb. *Normal Sulphite also reacts completely with Nitrous Acid.*

Replacing the pyrosulphite used in the last experiment by the normal sulphite, it was found that again hydroximidosulphate and a very little nitrilosulphate were precipitated, but in this case gradually. Here, however, potassium nitrite proved to be an additional product, which by gradually replacing the potassium sulphite in the solution allowed the process to be carried very far towards completion. The reaction is expressed by the equation  $3\text{HNO}_2 + 2\text{K}_2\text{SO}_3 = 2\text{KNO}_2 + \text{H}_2\text{O} + \text{K}_2\text{HNS}_2\text{O}_7$ , from which it is seen that only one-third of the nitrous acid becomes sulphonated, the rest being used up simply as an acid.

This interaction is what, we believe, Raschig must inadvertently have got, when seeking to prepare Pelouze's salt (hyponitrososulphate) by the use of nitric oxide. The conditions are favourable to the production of the nitrito-hydroximidosulphate (this vol., p. 439).

### IIIc. *Action of Sulphur Dioxide on Normal Sulphite and Nitrite.*

It has been shown in this paper (sect. Ib) that the hydroximidosulphate which, from the first, accompanies the normal sulphite as a product of the action of sulphur dioxide on alkali nitrite and hydroxide, occurs in small proportions until nearly all the hydroxide has been saturated. After that point is passed, and when, therefore,

sulphur dioxide is meeting a mixture of nitrite and normal sulphite, examination of the solution, by the method already described, shows that, along with a greater production of hydroximidosulphate than before, pyrosulphite is also produced in no insignificant quantity. This remarkable increase in the quantity of pyrosulphite, taken along with the fact (sect. IIa) that it acts on nitrite, proves that much of the sulphur dioxide combines directly with the normal sulphite.

It is only after the greater part of this salt has been converted into pyrosulphite that the sulphur dioxide sulphonates the nitrite, which it then does by combining with it in conjunction with the pyrosulphite, thus:  $2\text{KNO}_2 + \text{K}_2\text{S}_2\text{O}_5 + 2\text{SO}_2 + \text{H}_2\text{O} = 2\text{K}_2\text{HNS}_2\text{O}_7$ , the hydroximidosulphate being produced in this way with much greater facility than by the pyrosulphite alone, because its production is not accompanied here by the regeneration of normal sulphite with its inhibitory effect on sulphonation (sect. IIa). In this change, it still holds true that it is nitrous acid itself which is sulphonated, the potassium leaving the nitrite to enter the sulphonate radicle, and being replaced by hydrogen.

Claus held that there could be no difference between the effect of submitting a nitrite to the action of a sulphite and that of mixing it with a solution of hydroxide and then treating it with sulphur dioxide. The contents of this section and section IIa show that there is an essential difference between the two.

#### IIIId. *Action of Carbon Dioxide and of an Acid Carbonate on Normal Sulphite and Nitrite.*

As might be expected, the gradual addition of one of the stronger acids to a solution of normal sulphite and nitrite leads to the formation of sulphazotised salts. But even carbon dioxide and the acid carbonates of the alkalis produce a similar effect. Concerning the action of carbon dioxide, we have nothing to add to what has been published in our first paper (Trans., 1887, 51, 661). Normal carbonates of the alkalis are inactive.

It is known that nitrites are not decomposed by carbon dioxide, and also that alkali carbonates are decomposed by pyrosulphites as freely at the mean temperature as by sulphur dioxide itself. Accordingly, we have found that potassium or sodium hydrogen carbonate dissolved along with excess of normal potassium or sodium sulphite, gives off carbon dioxide to a current of air to about the same extent as it does in aqueous solution. But sodium hydrogen carbonate may be added to an ice-cold solution of sodium pyrosulphite, containing also much normal sulphite, and be only very gradually decomposed with effervescence. Indeed, an ice-cold concentrated solution of normal sodium

sulphite will deposit some acid carbonate when charged with carbon dioxide.

It is, therefore, not surprising that sodium or potassium hydrogen carbonate has a very marked action on mixed normal sulphite and nitrite. When the three salts are left together in solution in a closed vessel for a day or two, much sulphazotised salt is formed, so that after the carbonate and excess of sulphite have been precipitated by baryta and barium chloride in presence of ammonium chloride, the filtrate from the precipitate, after boiling with acid, gives much barium sulphate, and reduces cupric hydroxide freely. The interaction of the salts may be expressed by the equation  $\text{KNO}_2 + 2\text{K}_2\text{SO}_3 + 3\text{KHCO}_3 = \text{K}_2\text{HNS}_2\text{O}_7 + 3\text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ , but since the two-thirds normal hydroximidosulphate is to a small extent converted by normal carbonate into a more nearly normal salt and acid carbonate (Trans., 1894, 65, 534), the change expressed by the above equation cannot proceed to completion.

### IIIc. *Action of Sulphur Dioxide on Normal Carbonate and Nitrite.*

When sulphur dioxide is added to 2 mols. of nitrite and 1 mol. of normal carbonate, until the solution becomes acid to lacmoid paper, the only products are hydroximidosulphate and carbon dioxide. This was long ago pointed out by us, and also that sulphite and acid carbonate are intermediate products, the latter of which separates for a time from concentrated solutions. We have made further experiments to ascertain the effect of the first portions of the sulphur dioxide in producing hydroximidosulphate, which, where alkali hydroxide is used, we have shown to be insignificant.

These experiments were carried out in the same way as those for testing the effect when sodium hydroxide is employed (Ic), but with the modification of making two pipettings each time instead of one, and of weighing both instead of merely measuring them. Then in the one we determined the sodium as sulphate, and used the result for calculating what fraction of the original solution the other quantity was in which we determined sulphite and sulphonates. We thus made ourselves independent of the change of volume during the reaction caused by loss of carbon dioxide and gain of sulphur dioxide. We found, in this way, admitting of no refined accuracy, that at a later sampling the solution contained, at most, as much as  $3\frac{1}{2}$  per cent. less sodium than at an earlier sampling, a difference, however, hardly large enough to need attention.

The flask for receiving the portion for the sodium determination was previously weighed empty, but that for the other portion was weighed containing some concentrated solution of sodium hydroxide,

placed there to arrest all action in the pipetteful dropped into it. The first portion, by the changes it underwent on standing, showed how necessary the sodium hydroxide was for fixing the composition of the solution at the time it was sampled; sometimes acid carbonate was deposited from it, sometimes hardly any; sometimes the precipitated acid carbonate slowly disappeared, sometimes it did not. The solution used contained 1 part of sodium nitrite in 4.64 parts of water, besides the calculated quantity of anhydrous sodium carbonate.

The results of the experiments showed that hydroximidosulphate was largely produced from the beginning in proportion to the sulphite also formed. Thus, in one experiment, when 25 per cent. of the sulphur dioxide required for complete sulphonation had been passed in, 55.3 per cent. of it had become sulphonate, the rest (44.7 per cent.) sulphite. When 53.6 per cent. of the sulphur dioxide required had been used, 74.9 per cent. of it had become sulphonate and 25.1 per cent. sulphite. In another closely comparable experiment, when 33.7 per cent. of the sulphur dioxide required had been absorbed, 62.7 per cent. of it had become sulphonate and the rest sulphite; when 44.4 per cent. of the whole had been used, 72.75 per cent. of it had become sulphonate; and when 62.2 per cent. of the whole had been used, 81.5 per cent. of it had become sulphonate. That is to say, as for the last statement, when 20.2 grams of sodium nitrite (with carbonate) had received 37.5 grams sulphur dioxide, 23.3 grams of this had become sulphonate and 14.2 grams had become sulphite.

Uniform results are here, however, as when hydroxide is used as the starting point, only obtained by uniform working, of which the following experiment is a good example. A solution of sodium nitrite and carbonate was divided approximately into one-fifth and four-fifths, and both portions were treated, as nearly as could be, alike, their unequal quantities making the only difference. The smaller portion, when it had received 20 per cent. of the full amount of sulphur dioxide, was found to contain 61.8 per cent. of it in the form of sulphonate, 38.2 per cent. of it as sulphite. The larger portion, having received 25 per cent. of the amount necessary for its full sulphonation, was found to have only 55.3 per cent. of it as sulphonate and 44.7 per cent. of it as sulphite, as already given; had we stopped here at 20 per cent. sulphur dioxide, as we did with the smaller portion, the difference would have been still more striking. The difference observed was due to the smaller portion having, in relation to its quantity, received sulphur dioxide four times more rapidly than the larger portion had, the stream of sulphur dioxide having been steady and very nearly alike in the two cases. The result was that local saturation was less checked by the agitation of the flask

in this case than when the much larger portion of solution was under treatment.

The lack of uniformity in the results here described does not affect in the least the evidence they afford that the sulphonation of nitrite in presence of carbonate differs greatly in its course from what occurs in presence of alkali hydroxide.

Respecting the formation and destruction of sulphite in the process, this salt was observed to be produced rapidly until in quantity it has become equivalent to about one-eighth of the sulphur dioxide needed for sulphonation of all the nitrite. Then, for a time, its quantity remains nearly steady, all the sulphur dioxide which enters the solution during that time becoming sulphonate. Finally, it steadily lessens in quantity as more sulphur dioxide is added, and disappears just at the end of the sulphonation. The more rapidly the sulphur dioxide is blown in at first, the less of it becomes sulphite, and the more sulphonate, as already stated above.

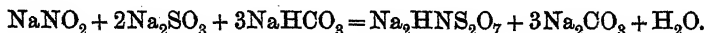
One other striking thing observed in these experiments was the great variability, not only of the point at which acid carbonate was first precipitated, but also of the quantity. With quick working, acid carbonate precipitated much earlier and in much larger quantity than in slow working; thus, whilst with quick working acid carbonate separated in abundance when 20 per cent. of all sulphur dioxide had been absorbed, it only precipitated, and then much less copiously, when 44 per cent., and in another experiment 53 per cent., of all the sulphur dioxide had been supplied more slowly. The main condition, therefore, for early precipitation of acid carbonate is rapid addition of the sulphur dioxide at first, the same condition as that which favours growth of sulphonate at the expense of sulphite.

*Discussion of the results.*—It becomes highly probable from a consideration of these results, together with what we know of the several substances concerned, that the first action or tendency to act of sulphur dioxide when it enters the solution is to convert carbonate into normal sulphite and acid carbonate, and to leave the nitrite untouched, and that this action remains prominent so long as much normal carbonate is undecomposed. Although this cannot be shown experimentally, it is certain that this action does take place, for its products present themselves freely, products which could not be derived from the sulphonation of the nitrite. Both normal sulphite and acid carbonate act together with sulphur dioxide in sulphonating nitrite.

In accordance with what is stated in sect. III*d*, the normal sulphite and acid carbonate together slowly disappear of themselves from the solution if the current of sulphur dioxide is stopped, owing to sulpho-



nation of the nitrite and reconversion of acid carbonate into normal carbonate,



Such a mode of sulphonation will therefore be also in operation when the entrance of more sulphur dioxide has not been arrested, but it is very slow in presence of normal carbonate, and may be disregarded as a factor in the process of sulphonating when sulphur dioxide is also at work. Here we would state that it is only to simplify discussion that we speak of normal sulphite and carbon dioxide, or even acid carbonate, being together unchanged; these substances, as previously stated, act on each other to a large extent in ice-cold solutions, and in our work we met with precipitated acid carbonate at times when it could only be there in consequence of carbonic acid withholding sodium from pyrosulphite.

That, in the earlier stages of the process, when much carbonate is present, the normal sulphite plays a very small part in the sulphonation, not only follows from the observation of the rapid increase in quantity at first, but is also shown by the quantity remaining nearly constant for a long time, although sulphur dioxide is still entering the solution and forming sulphonate. Only later, as the carbonate becomes consumed, does the sulphite become an important factor in the sulphonation by freely becoming pyrosulphite, for then its quantity rapidly falls.

The part played by sulphite in the early stages being thus insignificant, we have to seek in the carbonates the source of the early considerable sulphonation of the nitrite. It would be unreasonable to assume, with acid carbonate present, that the normal carbonate takes part in sulphonation: equally so to assume that it remains inactive to sulphur dioxide. We are therefore compelled to recognise that sulphonation goes on only after the conversion of all the carbonate *locally* present to acid carbonate and normal sulphite has been effected. Then the reaction that ensues is represented by the equation,



When all normal carbonate has been converted into the acid salt by the carbon dioxide, the sulphite becomes as active as the acid carbonate, and neither salt gets consumed before the other.

Whilst it seems certain that first the sulphur dioxide converts the normal carbonate into normal sulphite and acid carbonate, and only then produces hydroximidosulphate by acting on the nitrite along with acid carbonate in the earlier stages, and on both this and normal sulphite collaterally in the later stages, the experimental results show that local saturation must take place largely at the point where the

sulphur dioxide enters the solution, as so much sulphonate is produced along with the sulphite. In consequence of the activity of acid carbonate, local saturation becomes twice as difficult to prevent as when hydroxide is used in place of carbonate.

If, in order to impede local saturation, we slacken the rate of passing the sulphur dioxide into the solution, we meet with a fair amount of success. Thus, it was shown by the results of experiments already given, that the slower rate gave proportionately less sulphonate and more sulphite. But the effect of slowness in passing in the gas has its limit, in consequence of the continuous, although slow, interaction which takes place between nitrite, normal sulphite, and acid carbonate, whereby sulphite disappears, to give place to sulphonate. It follows that too slow, as well as too rapid, an addition of sulphur dioxide is unfavourable to the accumulation of sulphite, rather than of sulphonate, in the solution, and that a medium rate of supply is best for raising the proportion of sulphite.

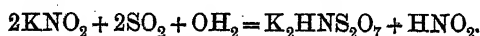
There remains to be explained the great variability in the commencement of precipitation of the acid carbonate. This takes place the sooner the faster the sulphur dioxide is blown into the solution. When it occurs in the earlier stages of the process, it is therefore accompanied by greater predominance than usual of production of hydroximidosulphate over production of sulphite. It does not, however, depend upon this, for whilst sulphur dioxide liberates 1 mol. of carbon dioxide in changing carbonate into sulphite, 4 mols. of it are needed to liberate 1 mol. of carbon dioxide in changing carbonate and nitrite into hydroximidosulphate.

An explanation is suggested by a consideration of the fact that, when working the process at a moderate rate, the first crystallisation of acid carbonate takes place long after the point at which the solution must contain the maximum of the salt, at least potentially, the point, that is, when half the carbonate has become either sulphonate or sulphite. When it does occur, the quantity of it in solution has become much less. Only where crystallisation is started early by a very rapid addition of sulphur dioxide does the acid carbonate continue to separate out in such quantity as it could do at the stage of the process reached. The cause in one word is supersaturation. The acid carbonate, it would seem, is slow to begin to precipitate from the solution while that is not charged with carbon dioxide. At a medium rate of working, this only happens in the later stages, any normal carbonate and even much normal sulphite present keeping down the quantity of carbon dioxide, but by a rapid rate of working local saturation occurs and the acidified portion of the solution then crystallises. Once crystallisation has been started, it proceeds unchecked. In slower working, when crystallisation only begins late in

the process, the amount of salt separating is small, and generally depends then for its existence upon its power to resist the action of acid sulphite in ice-cold solutions. The solution when, potentially, at least, it is richest in acid carbonate, was found by us to crystallise soon if left to stand in a closed vessel, although sulphonation, which is destructive of acid carbonate, was slowly going on in it.

### III*f*. Primary Action of Sulphur Dioxide on a Nitrite.

Solution of sulphur dioxide added to that of potassium or sodium nitrite produces a sulphate and either nitric or nitrous oxide, according as one or other of the interacting substances is in excess. That is the ordinary well-known result, but there are two ways of limiting the extent of the action so as to obtain either hydroximidosulphate and nitrous acid, or the undoubted products of their transformation. In this way, it is shown that the interaction of sulphur dioxide and a nitrite is



The more important way to thus limit the action is by an experiment first tried by Claus (*Ber.*, 1871, 4, 508; this vol., p. 437), which consists in adding an alcoholic solution of sulphur dioxide to excess of potassium nitrite in strong aqueous solution. For this experiment gives, as we have ascertained, potassium nitrito-hydroximidosulphate which precipitates, and ethyl nitrite, which boils off by the heat of the reaction,  $3\text{KNO}_2 + 2\text{SO}_2 + \text{C}_2\text{H}_5\cdot\text{OH} = \text{KNO}_2 + \text{K}_2\text{HNS}_2\text{O}_7 + \text{C}_2\text{H}_5\text{NO}_2$ . By becoming ethyl nitrite, the nitrous acid is rendered inactive towards the hydroximidosulphate, which is thus saved from oxidation.

The other way of tracing the earlier action of sulphur dioxide on a nitrite was found out by Raschig when trying to prove another point (sect. IV*a*). He added the nitrite to excess of sulphur dioxide, both being in very dilute and well cooled solution, evaporated down and neutralised the solution with chalk, and again evaporated the filtered solution. After much potassium sulphate had crystallised out, potassium amidosulphate was finally obtained, as proof that hydroximidosulphate had been formed at an earlier stage. Our own experiments have yielded us an earlier product of the degradation of this compound.

At the time when Raschig published his observation, we published (*Trans.*, 1887, 51, 659) one of ours, that silver nitrite and mercurous nitrite, when decomposed by sulphur dioxide solution, yield a substance answering to the copper test for hydroxylamine. This we now know to be hydroxyamidodisulphuric acid, but at the time we took it to be hydroxylamine itself. We have also found that, after adding a dilute solution of sodium nitrite to excess of a cooled solution of sulphur dioxide and

then blowing out of the solution the residual sulphur dioxide by a current of air, enough hydroxyamidodisulphate (hydrolysed hydroximidosulphate) is present to be easily identified by the copper test. A hydroxyamidodisulphate is distinguishable from hydroxylamine in applying this test by finding that the mother liquor of the cuprous oxide (which need not be filtered off) gives sulphurous acid when acidified (Trans., 1889, 55, 770).

Although less successful than Claus's experiment, Raschig's method is serviceable for showing that the alcohol used in the former plays only a secondary part. Whilst excess of nitrite is successfully used in that experiment, the sulphur dioxide must be in excess in Raschig's method. To understand this, it has only to be remembered, firstly, that nitrous acid would oxidise hydroximidosulphate at once, and, secondly, that sulphurous acid sulphonates the hydroximidosulphate slowly enough to allow a little of it being secured in a hydrolysed state.

#### *IVa. Sulphonation of Nitrous Acid by Sulphurous Acid.*

Freymy believed that certain of his sulphazotised salts were formed in the first action of sulphurous acid on nitrous acid. From this belief, Claus strongly dissented, holding that presence of a base (as salt) was essential to the production of these acids. Raschig considered that his experiment of treating potassium nitrite with sulphur dioxide in excess (sect. III f) proved the correctness of Freymy's belief; but that cannot be admitted, since potassium is present in this experiment playing the part of base. It is, however, quite practicable to establish Freymy's belief, that no base whatever is necessary to bring about the formation of sulphazotised acids.

When a solution of sulphur dioxide, better ice-cold, is treated with a relatively small quantity of nitrous fumes passed on to its surface while it is being well agitated in a flask, and is then deprived of the remaining sulphur dioxide by a rapid current of air, or even by quick boiling, it will give a good reaction for hydroxyamidodisulphuric acid with the copper test. A little deviation in the composition of the nitrous gas from that of nitrogen trioxide is not of importance. If the object is only to get amidodisulphuric acid, the solution of sulphur dioxide is left to stand for a day after it has received the nitrous acid, without expelling what is left of the sulphur dioxide. If it is then evaporated on the water-bath, and further concentrated in the vacuum desiccator, the amidodisulphuric acid will crystallise out from the sulphuric acid by which it is accompanied (Trans., 1896, 69, 1634). We have purified the acid by recrystallisation, and have hydrolysed it at 150°,

by means of hydrochloric acid, into acid ammonium sulphate; we have also completely volatilised the acid by heat, thus proving the absence of base accidentally derived.

Nitrosyl sulphate dropped into a large excess of cooled solution of sulphur dioxide also yields the hydroxyamidodisulphate reaction with copper sulphate and potassium hydroxide.

#### *IVb. Influence of the Base of the Nitrite or Sulphite.*

Although Fremy held that sulphurous and nitrous acids combine together, he did not believe that the resulting sulphazotised acids could be obtained in this way, because of their inability to exist in absence of a base. Moreover, he considered that a strong base is influential in bringing about the formation of these acids, although he was not successful when employing soda as the base. The only hydroximidosulphates he could isolate, indeed, were those of potassium, but from ammonium nitrite he prepared the nitrilosulphate, and also obtained evidence that calcium, strontium, and barium nitrites are convertible into amidated sulphates.

We have just shown (sect. IVa) that the interaction of sulphurous and nitrous acids does not require the presence of a base in order to produce sulphazotised acids, although such presence is essential to preserve unchanged the first product of the interaction. Some bases will doubtless be inferior to others for this purpose, and those which do not freely form soluble pyrosulphites are difficult to work with; otherwise the nature of the base seems to be a matter of indifference. Since the time of our early publications on the subject, we have extended our experiments to several other nitrites than those of sodium, mercurous, and silver, with the results we now record.

*Ammonium Salts.*—Ammonium nitrite solution was prepared by triturating silver nitrite with its equivalent of ammonium chloride dissolved in about five times its weight of water, and removing silver chloride with the aid of the pump, and to the filtrate, after it had been cooled in ice, was added a little less than its equivalent of ammonia, which had just before been converted into sulphite by passing sulphur dioxide into the solution; more sulphur dioxide was then passed into the mixture until it reddened lacmoid paper. In this way, the ammonium nitrite was almost all sulphonated without any evolution of gas having occurred until just at the last, when slight nitrous fumes appeared. Some of this solution, on being hydrolysed and then tested with copper sulphate and potassium hydroxide, was shown to have contained abundance of ammonium hydroximidosulphate. Another portion of the solution not hydrolysed gave a large precipi-

tation of two-thirds normal potassium hydroximosulphate on adding potassium chloride.

*Barium Salts.*—Some barium hydroxide was converted into sulphite by putting it in water and passing in sulphur dioxide; the barium sulphite was then, for the most part, brought into solution by passing in more sulphur dioxide. The product was added gradually to a solution of a little more than its equivalent of barium nitrite, but having neglected to cool our solutions we feared that our experiment was a failure, for not only was there a large precipitate but also a considerable evolution of nitrous gases. For our purpose, however, we found we had been amply successful; the solution was only faintly acid to litmus and remained so for hours, both it and the precipitate containing large quantities of barium hydroximosulphate. The precipitate also contained sulphite and sulphate, the latter being the complement to the nitrous fumes produced. The hydroximosulphate was extracted from the precipitate by a solution of ammonium chloride.

*Calcium Salts.*—A solution of calcium nitrate, free from magnesium, sodium, potassium, and other ordinary impurities, was heated with well-washed, spongy lead until nitrogen oxides and ammonia began to form, and the filtered, very alkaline solution was first freed from lead by hydrogen sulphide, not used in excess, and then the calcium hydroxide was removed by carbon dioxide. (It was interesting to find that, contrary to assertion, carbon dioxide cannot be used to precipitate lead in presence of a calcium salt, since calcium precipitates before lead.) A solution of calcium sulphite in sulphurous acid was prepared just before use, in the same way as the barium salt had been, except that carefully prepared calcium carbonate took the place of barium hydroxide. Employing the calcium nitrite somewhat in excess of the calcium sulphite, the solution of the latter was gradually poured into the former, both solutions having ice floating in them at the time. No gas was given off, and only a moderate quantity of precipitate was formed, which consisted of sulphite. The filtrate was neutral and contained the full quantity of hydroximosulphate expected.

*Zinc Salts.*—Zinc nitrite solution was prepared by precipitating zinc sulphate with barium nitrite and filtering. Zinc sulphite in solution in sulphurous acid was made from zinc oxide in water and sulphur dioxide. The two solutions, suitably proportioned and with ice floating in them, were mixed. No gas came off, zinc sulphite was precipitated, and the solution contained zinc hydroximosulphate in large quantity.

*Mercurous Salts and Silver Salts.*—Experiments, already referred to in section III of this paper, sufficiently establish that mercurous and silver nitrites are readily sulphonated. It is now evident that the sulphonation of nitrites is a general reaction, essentially independent

of the nature of the base, which only effects the preservation of the products. It is not the salts which are sulphonated, but nitrous acid itself.

V. *What Nitrous Acid becomes when Sulphonated.*

In our paper on the non-existence of dihydroxylamine derivatives (this vol., p. 432) it has been established that neither theoretical considerations nor the abundant experimental work of other chemists and ourselves afford any support to the view that the double sulphonation of nitrous acid into a hydroximidosulphate occurs in two stages, or that a monosulphonated nitrous acid,  $\text{ON}\cdot\text{SO}_3\text{H}$  or  $(\text{HO})_2\text{N}\cdot\text{SO}_3\text{H}$ , must be the first product of its change. In the present communication, it is shown that the acidity necessary for the sulphonation of a nitrite points clearly to the fact that it is in every case the acid itself, and not its salts, which is directly sulphonated. We are, therefore, in the position to affirm that the fundamental interaction in the formation of all Fremy's sulphazotised salts is that between actual nitrous acid and a pyrosulphite in which there is always formed the one substance, the two-thirds normal hydroximidosulphate corresponding to the pyrosulphite acting, thus:  $\text{HONO} + (\text{SO}_2\text{K})\cdot\text{SO}_3\text{K} = \text{HON}(\text{SO}_3\text{K})_2$ . The origin of all the other salts out of this salt has been traced, partly by others and partly by ourselves, and need not be gone over again here.

LVII.—*Presence of Invertase in some Plants of the Gramineæ. Part I.*

By JAMES O'SULLIVAN.

IN 1890) *Trans. Laboratory Club*, 3, 5), I drew attention to the presence of invertase in the rootlets and plumules of germinated barley; the object of the present paper is to prove that this enzyme is common to other and more mature plants of the *Gramineæ*.

The difficulty of extracting enzymes from the living cells of plants is now well known: even healthy yeast, as I have shown (*Trans.*, 1892, 61, 593), does not give up its invertase to water. The extraction of invertase from the plants under consideration is not necessary, however, if it is proved satisfactorily that there must be a substance within the cells of these plants which has the power of hydrolysing cane-sugar.

*Extraction of Invertase from Maize and Oat Plants.*

I have succeeded in preparing from maize and oats a small quantity of a substance which had an undoubted, although slight, hydrolytic action on cane-sugar. The method employed was as follows. Three healthy maize plants, grown in the open and about 12 inches high, were carefully uprooted and the roots cut off. The leaves and culms were cut up into small pieces, which were then well washed with recently distilled water containing chloroform. The pieces were ground with silver sand, left in contact with chloroform water for 24 hours, and then filtered. Alcohol was added to the filtrate until no further precipitation occurred, the precipitate being then collected on a filter and dried over sulphuric acid in a vacuum; only 0.135 gram of substance was isolated. In like manner, from eight strong oat plants, I obtained only 0.04 gram of substance.

Two small test-tubes, each containing 10 c.c. of a 5 per cent. cane-sugar solution, were plugged with cotton wool, sterilised, and cooled. A drop of chloroform and the whole of the substance from maize was put into one of the tubes, *a*, and into the other, *b*, the same amount of chloroform and the substance from oats. After remaining for 4 days in the cold, the solutions were carefully neutralised with potassium hydroxide and boiled for some time. The cupric oxide reducing power, *K*, of the solutions was determined gravimetrically, and the amount of cane-sugar hydrolysed calculated on the weight of substance used,\* was, for *a*, 44 per cent., and *b*, 50 per cent.

*Existence of Invertase in Roots and Leaves of Oats, Maize, and Wheat.*

*Oats.*—Some oat grains were steeped in water for 48 hours, and then grown in moist sand. On the seventh day of growth, the roots and plumules were removed from 20 of the germinated grains. The roots weighed 0.25 gram, and the plumules 0.47 gram. These were washed with chloroform water, dried between filter paper, and added each to 10 c.c. of a 5 per cent. solution of cane-sugar saturated with chloroform.† After remaining for 18 hours at 15–18°, they were then removed by filtration, and washed until the filtrate and washings amounted to about 50 c.c. After neutralising, as above mentioned, the solutions were briskly boiled for some time, and the value of *K* for each determined, with the following results, expressed as before:

Roots = 33.1 per cent.; plumules = 14.7 per cent.

\* All the expressions for the invertase are calculated throughout this paper in this manner.

† The cane-sugar solution throughout this paper means a 5 per cent. solution saturated with chloroform.



The residual roots and plumules were immediately immersed in the same quantity of cane-sugar solution, and treated in every way as just described. The results obtained in this second treatment were:

Roots = 10.7 per cent. ; plumules = 9.3 per cent.

When the oat seedlings had grown for some time, the leaves being about 5 inches long and the endosperm consumed, some of the leaves were cut off at their junction with the leaf-sheath. These weighed 0.831 gram; they were divided equally by weight, and the two portions washed several times with chloroform water, and finally dried by pressure between filter paper. One part, *a*, was added to 10 c.c. of a water solution of chloroform, and the other part, *b*, to 10 c.c. of the sugar solution. After remaining for 18 hours at 15—18°, these were treated as already described, and the results obtained, expressed as before, were:

*a* = none ; *b* = 24 per cent.

The leaves used in *a* and in *b* were then immersed separately in 10 c.c. of the sugar solution, and, after remaining for 18 hours at 15—18° were treated as before, with the results:

*a* = 34 per cent. ; *b* = 16 per cent.

*Maize*.—Two maize plants, with the endosperm still attached, which were growing in the open, were carefully uprooted. The plumules and roots were cut off at their junction with the seed. The former weighed 0.43 gram, and the latter 0.24 gram. These were treated in every particular as in the case of the oat plant, and the results were:

Plumules = 16.7 per cent. ; roots = 14.9 per cent.

They were immediately immersed in the same quantity of the cane-sugar solution, digested under the same conditions, and treated in every way as in the last instance. The results obtained in this second treatment were:

Plumules = 10.0 per cent. ; roots = 22.0 per cent.

Two maize plants like those just described were similarly divided at the time. The plumules weighed 0.486 gram, and the roots 0.096 gram. These were each immersed in 10 c.c. of chloroform water, and at the end of 18 hours the extracts had no cupric reducing power. The plumules and roots from these experiments were each added to 10 c.c. of the sugar solution and digested as before at 15—18° for 18 hours, with the following results:

Plumules = 13.0 per cent. ; roots = 20.0 per cent.

*Wheat.*—Two quantities, each weighing 0.38 gram, of the seedling leaves of wheat were taken. To one, *a*, 10 c.c. of chloroform water were added, and to the other, *b*, 10 c.c. of the sugar solution. After 18 hours at 15–18°, the results obtained were:

$$a = \text{none}; b = 52 \text{ per cent.}$$

The leaves from *b* were immediately immersed in the same quantity of the sugar solution, and the result obtained, expressed as before, was 54 per cent.

A quantity of the portion of wheat seedlings above ground was collected during a period of snow and severe frost, and divided into four parts of 1.3 grams each. After washing with chloroform water and drying as already mentioned, three of the parts, *a*, *b*, and *c*, were each added to 15 c.c. of the cane-sugar solution, and the fourth, *d*, to the same volume of chloroform water; all were digested for 24 hours in the cold; the results obtained were:

$$a = 8.9; b = 10.0; c = 10.9; d = 0.35 \text{ per cent.}$$

In order to compare with *a*, *b*, and *c*, the result obtained in *d* is expressed in terms of cane-sugar hydrolysed, as if cane-sugar had been present.

Four days after the last series of experiments were made, the weather having in no way improved, another quantity of the wheat plants was collected and divided into two parts of 0.354 gram each. One part, *a*, was treated as in the last series of experiments, and the second, *b*, as *a*, only it was digested at 49–50°. The results were:

$$\begin{array}{ll} a, & 24 \text{ hours at laboratory temperature, } 8.1 \text{ per cent.} \\ b, & 3 \text{ hours at } 49\text{--}50^\circ \dots\dots\dots 6.3 \text{ } \end{array}$$

The residue from *b* was again treated as before for 3 hours and gave 4.7 per cent.

This residue was treated in the same way for 16 hours, and gave 29.4 per cent.

In order to test how much of the cane-sugar, in the presence of the chloroform, would be hydrolysed at a temperature of 50°, the same quantity of the cane-sugar solution as used in the last series of experiments was digested for 24 hours at this temperature, and, calculated from the value of *K* obtained, the cane-sugar hydrolysed amounted only to 0.002 gram.

The total quantity of sugar, calculated as dextrose, in some of the same wheat leaves as used in the last series of experiments was determined, and amounted to 0.72 per cent.

*Hydrolysis of Cane-sugar not due to Organisms attached to the portions of Plants employed.*

In 1890, I concluded that organisms were not the cause of the inversion of the cane-sugar under the conditions of my experiments, and further proof of this view may now be given.

Some wheat plants were collected under the conditions already mentioned, and of these 4 grams were washed several times with small quantities of chloroform water until the total washings amounted to 250 c.c. To these washings, which were turbid, a little aluminium hydrate was added, and after well stirring, the whole was put aside in a tall cylinder for 24 hours; the supernatant liquid was then poured off and the deposit, *e*, retained. Microscopically, no organism could be detected in this deposit.

Seven of the same plants of equal size were chosen and the leaves cut from the culm of each were equally divided numerically into two portions, *a* and *b*, weighing respectively 0.29 and 0.301 gram. The seven culms, *c*, weighed 0.138 gram. The leaves, *a* and *b* separately, were washed with chloroform water, in small quantities at a time, until the washings in each case amounted to 500 c.c. To the 1000 c.c. of washings thus obtained, some Swedish filter-paper pulp was added, and after stirring well, the whole was filtered through a small filter paper, which, with its pulp contents, may be designated *d*.

The deposit, *e*, the leaves, *a* and *b*, the culms, *c*, and the filter paper, *d*, with its contents were each added to 15 c.c. of the sugar solution and digested for 6 hours at 49—50°. The results as expressed before were:

$$a = 16.5; b = 12.0; c = 13.1; d = 0.06; e = 0.05 \text{ per cent.}$$

The results obtained in *d* and *e* are given in terms of cane-sugar hydrolysed, calculated on the quantity of leaves which was washed.

*Existence of Invertase in the Roots and Leaves of a nearly mature Maize Plant.*

A maize plant about 16 inches in height and upon which the reproductive organs had not as yet appeared, was carefully uprooted in June, 1893. The weight of the leaves and culm was 8.26 grams, and that of the roots 0.841 gram.

The roots were divided into two equal parts, *a* and *b*, of 0.42 gram; each part was well washed with chloroform water, dried by pressure between filter paper, and added to 25 c.c. of cane-sugar solution. After remaining for 18 hours in the cold, the extent of hydrolysis was:

$$a = 26 \text{ per cent.}; b = 24 \text{ per cent.}$$

These roots were then added each to 10 c.c. of cane-sugar solution, and after remaining for 18 hours the results were :

$$a = 38 \text{ per cent. ; } b = 35 \text{ per cent.}$$

The leaves of the plant were divided by cutting lengthways through the midrib, and from the halves thus made strips were cut at right angles to the midrib. Three equal portions of 2.02 grams were taken, and to one, *a*, 25 c.c. of a 5 per cent. cane-sugar solution and 0.1 c.c. of chloroform were added, to another, *b*, a similar quantity of sugar solution, and to the third, *c*, the same volume of chloroform water.

After remaining 18 hours in the cold, the numbers, calculated as before, were :

$$a = 10 \text{ per cent. ; } b = 5 \text{ per cent. ; } c = 0.94 \text{ per cent.}$$

These leaves were treated as before and the results obtained were :

$$a = 10.7 \text{ per cent. ; } b = 7.1 \text{ per cent. ; } c = \text{nil.}$$

A leaf was selected on an almost mature maize plant and a section of the midrib weighing 0.631 gram was cut out lengthways and divided into pieces which were washed with a small quantity of chloroform water and then dried as in the experiments mentioned. After remaining 48 hours in the cold with 10 c.c. of a 10 per cent. cane-sugar solution, the amount of sugar hydrolysed was 12.1 per cent.

A similar portion of the midrib of the same leaf, which was still attached to the growing plant, was cut out two days later. This weighed 0.295 gram, and, treated as in the last instance, the result indicated hydrolysis to the extent of 7.5 per cent.

To similar quantities of cane-sugar solution, the washings from the portions of midrib used in these experiments were separately added, and after digesting for the same time, the solutions were found to have no cupric oxide reducing power.

### LVIII.—*Mannogalactan and Lævulomannan. Two New Polysaccharides.*

By JULIAN LEVETT BAKER and THOMAS HENRY POPE.

It is well known that uncrystallisable carbohydrates other than the starches occur in the endosperm of many seeds and nuts. The examination of such carbohydrates is a matter of some difficulty, because they are in general very stable substances, and the methods of attacking them are consequently limited.

The investigations of E. Schulze, Steiger, Maxwell, Reiss, and

others have shown that the cell-wall of the endosperm of many seeds and nuts contains not only a substance which is insoluble in dilute acids, and, from its general behaviour, is considered to be cellulose, but also certain carbohydrates which are quickly dissolved and decomposed by hot dilute acids, yielding galactose, mannose, and pentoses. Several representatives of this group of carbohydrates, for example, galactoaraban, galactoxylan, galactomannan, and certain less complex galactans and mannans have been already described, and these differ from true cellulose by their indifference towards iodine and their insolubility in cuprammonium hydroxide. Very little attention has been paid to these compounds, which are usually obtained by extracting the seeds or nuts with dilute aqueous alkali, and in some cases with water alone; the main point which has been recorded in connection with their chemical behaviour is the fact that, on hydrolysis with enzymes or dilute acids, they yield certain sugars which have been identified by ordinary methods.

In the present communication, we describe an examination of the reserve carbohydrates derived from the endosperm of the Indian clearing nut (*Strychnos potatorum*) and the ivory nut (*Phytelephas macrocarpa*). Although these substances perform the functions of reserve material for the embryo, we have not been able to investigate the action on them of the particular enzymes associated with them in the nuts, and have therefore been obliged to confine ourselves almost entirely to a study of the products of hydrolysis by acids. In the case of the former, these products consist of galactose and mannose, and of the latter, mannose and lævulose, the two complex carbohydrates, as will be shown later, presenting well-marked differences in their physical and chemical properties. According to the nomenclature adopted by E. Schulze (*Ber.*, 1891, 24, 2227), the carbohydrate from the clearing nut should be classed as a galactomannan or mannogalactan, that from the ivory nut being a lævulomannan or mannolævulan. Such names, however, take no account of the relative amount of each sugar obtained on hydrolysis, and in view of the fact that the substance derived from the clearing nut yields considerably more galactose than mannose on hydrolysis, we propose to call it a *mannogalactan*; on similar grounds, the carbohydrate obtained from the ivory nut is referred to as a *lævulomannan*. With regard to the last-named substance, it is noteworthy that lævulose, although in small amount, constitutes one product of hydrolysis; so far as we are aware, inulin, cane-sugar, and melibiose are the only well-known carbohydrates which, on hydrolysis, give rise to lævulose.

## MANNOGALACTAN.

According to the *Dictionary of Economic Products of India* (1893, 6, iii, 382), the clearing nut constitutes the stone of the fruit of a tree widely distributed throughout India; when soft, it is grated, and in this state is made use of for clearing muddy water contained in earthenware vessels. In order to obtain the nuts in a condition suitable for investigation, they were soaked in water at 35° for two days and then passed through a mincing machine; the product was dried in air, and finally ground in a coffee mill.

The finely divided nuts were soaked in water, and then heated in a water-bath with 5 per cent. sulphuric or oxalic acid for 5 hours. The greater portion dissolved, leaving a residue apparently consisting chiefly of cellulose. The acid liquid was neutralised with precipitated calcium carbonate, boiled with animal charcoal, filtered and evaporated under diminished pressure until the residue became syrupy. Alcohol was stirred into the syrup, and in the course of a few days a solid magma of crystals was obtained. The whole of this product was then triturated with a mixture of ethyl and methyl alcohols and filtered, the crystalline portion being purified by recrystallisation from 90 per cent. alcohol. By this means, a sugar was obtained which separated in aggregates of hexagonal prisms melting at 160—163°; the mean of three determinations of the specific rotatory power in 4 per cent. aqueous solution gave  $[\alpha]_D + 79.7^\circ$ . The product was identified as galactose; its phenylhydrazone melted at 156°, and it gave mucic acid on oxidation with nitric acid.

The mother liquor from which the galactose had been removed was freed from alcohol and treated in the cold with phenylhydrazine acetate. In a few minutes, a phenylhydrazone separated, crystallising from hot water in faintly yellow, rhombic plates melting at 186°. Mannose phenylhydrazone melts at 186—188° (Reiss, *Ber.*, 1889, 22, 609).

The clearing nut therefore contains a substance which, on hydrolysis with acids, yields a mixture of galactose and mannose. The absence of pentose sugars was proved by means of the furfuraldehyde test.

*Isolation of Mannogalactan.*

Attempts were made to isolate this substance from the ground nuts by extraction with hot 2 per cent. aqueous alkali. The extract was filtered, acidified with acetic acid, boiled with animal charcoal, and then filtered into strong alcohol. The white, flocculent precipitate which separated was collected, redissolved in water, and again poured into a large volume of alcohol. The freshly precipitated substance was

filtered, washed with 95 per cent. alcohol, dried at  $110^{\circ}$ , and cooled in a vacuum; after this treatment, the specific rotatory power of a 2 per cent. solution was  $[\alpha]_D +75.1^{\circ}$ , allowance being made for ash, which amounted to upwards of 2 per cent. Owing to the difficulty of removing mineral constituents, this method of preparation is, however, unsatisfactory.

It was found that mannogalactan could be precipitated from moderately concentrated aqueous solutions by glacial acetic acid. The precipitate thus obtained was filtered and washed, first with cold, then with hot, alcohol and finally with ether; in order to remove the last traces of acetic acid, the product was extracted with strong boiling alcohol and then washed on the filter with cold 95 per cent. alcohol. The snow-white substance was dried in air and then heated at  $105^{\circ}$  for several hours, being afterwards allowed to cool in a vacuum. It contained 0.27 per cent. of ash and had the specific rotatory power  $[\alpha]_D +71.5$  in a 2.5 per cent. aqueous solution.

Although this method yields a product which contains a comparatively small proportion of inorganic constituents, the process itself is somewhat tedious, and necessitates the employment of considerable quantities of alcohol. We have therefore been led to adopt a method of purification which depends on the fact that the mannogalactan from the Indian clearing nut forms a voluminous blue precipitate with Fehling's solution or with cuprammonium hydroxide. The precipitate can be readily washed, provided the liquid remains slightly alkaline, but on reducing the alkalinity below a certain limit, the precipitate becomes soluble in water. The isolation of a mannan from yeast by means of the copper compound has been effected by Salkowski (*Ber.*, 1894, 27, 497). The method we adopted consisted in treating the ground nuts with a 2 per cent. solution of caustic soda for 2 hours in a water-bath, filtering through glass wool, and adding excess of Fehling's solution to the filtrate. The blue precipitate settles to a pasty mass, excess of copper salt and other impurities being removed by kneading and washing with water. Cold dilute hydrochloric or acetic acid is added to decompose the copper compound, the light green solution thus obtained being filtered and poured into strong alcohol. The white precipitate is washed with cold and then with hot alcohol, again dissolved in water, and reprecipitated with alcohol. The product is collected, dried in the air, then at  $105^{\circ}$  and cooled in a vacuum. This method of preparation gives excellent results, a neutral, ash-free substance being obtained; it is of great value for the isolation in a pure condition of the polysaccharides we have examined, and its application to the study of certain other complex polysaccharides foreshadows results of an interesting nature.

The mannogalactan obtained by any of these three methods is a

snow-white, amorphous substance sparingly soluble in cold water, but very soluble in dilute caustic alkali. It gives no colour reaction with iodine.

In order to satisfy ourselves that we were dealing with a homogeneous substance, some of the mannogalactan ( $[\alpha]_D + 67.1^\circ$ ) was dissolved in water and fractionally precipitated with alcohol. Some difficulty was experienced in doing this, owing to the extreme insolubility of the mannogalactan in alcohol. Two fractions were, however, obtained which had the specific rotatory powers  $[\alpha]_D + 68.8^\circ$  and  $+ 67.3^\circ$  respectively, showing that a separation had not been effected. On analysis:

0.2239 gave 0.3620  $\text{CO}_2$  and 0.1266  $\text{H}_2\text{O}$ .  $\text{C} = 44.11$ ;  $\text{H} = 6.28$ .

0.1971 „ 0.3200  $\text{CO}_2$  „ 0.1112  $\text{H}_2\text{O}$ .  $\text{C} = 44.29$ ;  $\text{H} = 6.27$ .

$\text{C}_6\text{H}_{10}\text{O}_5$  requires  $\text{C} = 44.40$ ;  $\text{H} = 6.11$  per cent.

A 3 per cent. aqueous solution is viscous, and it is therefore necessary to conduct the polarimetric examination in dilute solutions.

0.7878 gram dissolved in 25 c.c. of water gave  $\alpha_D + 2.34^\circ$  in a 100 mm. tube at  $15^\circ$ , whence  $[\alpha]_D + 74.2^\circ$ .

0.6222 gram and 0.6592 gram, under similar conditions, gave  $\alpha_D + 1.85^\circ$  and  $\alpha_D + 1.96^\circ$  respectively, whence  $[\alpha]_D + 73.9^\circ$  and  $74.3^\circ$ .

#### *Hydrolysis of Mannogalactan.*

Attempts were made to hydrolyse this substance with precipitated diastase and with yeast invertase, both at their optimum temperatures and in the cold, but without success. The nuts refused to germinate, and we were thus unable to obtain any active enzyme which would hydrolyse the contents of the endosperm. A number of inversions were carried out with oxalic, sulphuric, and hydrochloric acids. From 0.5 to 1 gram of the substance was dissolved in water, treated with acid until enough had been added to raise the concentration to 2 per cent., and the acid liquid then heated in a bath of boiling water during 20 or 30 minutes. The inverted solution was cooled to  $15^\circ$ , diluted to 25 c.c., and the rotation observed in a 200 mm. tube, the specific rotatory power of the mixed sugars being  $[\alpha]_D + 58.8^\circ$ , as the mean of ten determinations. As the sole products of hydrolysis of mannogalactan are galactose and mannose, the value  $[\alpha]_D + 58.8^\circ$  represents the mean sum of the rotations of these two sugars. Taking Alberda van Ekenstein's number for the specific rotatory power of mannose, namely,  $[\alpha]_D + 14.25^\circ$  (*Rec. Trav. Chim.*, 1896, 15, 221), and that of galactose as  $[\alpha]_D + 80^\circ$ , a mixture of 2 mols. of galactose with 1 mol. of mannose would have the specific rotatory power  $[\alpha]_D + 58.04^\circ$ , a number in close agreement with the mean of our determinations.



The amount of galactose in the mannogalactan was then estimated by oxidising with nitric acid and weighing the mucic acid so produced (Tollens, *Annalen*, 1885, 227, 223; Creydt, *Ber.*, 1886, 19, 3115). In three determinations, the mucic acid obtained corresponded with 80, 82, and 77 per cent. of galactose. Three mols. of a substance having the empirical formula  $C_6H_{10}O_5$  should yield 2 mols. of galactose or 74 per cent. These results are not in very close agreement, but the method itself is far from satisfactory. It must be borne in mind that the evidence afforded by the mucic acid test is only qualitative in character; it serves, however, to indicate whether the ratio of the amounts of mannose and galactose in the inverted mannogalactan is 1 : 2 or 1 : 3.

Under the conditions of our experiments, it was not found possible to estimate the mannose as phenylhydrazone in presence of so large a quantity of galactose, because the separation of mannose phenylhydrazone from dilute solutions is incomplete.

Considering the data obtained from the inversion numbers, and their approximate confirmation by means of the mucic acid test, it may be concluded that the complex mannogalactan splits up on hydrolysis into one part of mannose and two parts of galactose.

In order to satisfy ourselves that the mannogalactan exists as such in the nut, and is not the product of the action of alkali, we extracted a quantity of the ground nuts with water. The extract, when cold, was precipitated with Fehling's solution and the resulting copper compound treated in the manner already described. The substance obtained by this means has in 2 per cent. aqueous solution the specific rotatory power  $[\alpha]_D + 72.5^\circ$ , and is in other respects identical with the preparations obtained by extracting the nuts with boiling dilute alkali. Hence the action of the alkali only serves to expedite the extraction of the polysaccharide.

#### *Derivatives of Mannogalactan.*

Although the polysaccharide forms an insoluble blue compound when treated in aqueous solution with either Fehling's solution or cuprammonium hydroxide, the copper compound could not be isolated in a condition suitable for analysis, for as the alkalinity of the liquid diminishes the compound becomes soluble. The addition of alcohol to the solution will then precipitate a copper compound, which is, however, not of constant composition.

Basic lead acetate precipitates from aqueous solutions of mannogalactan a compound containing varying proportions of lead.

*Dibenzoylmannogalactan*,  $C_6H_5O_5(CO \cdot C_6H_5)_2$ , is obtained on treating the mannogalactan with benzoyl chloride according to Baumann's conditions (*Ber.*, 1886, 19, 3218). It is a white, amorphous substance

with an indefinite melting point, and is soluble in glacial acetic acid, alcohol, or benzene. On analysis:

0.1905 gave 0.4495  $\text{CO}_2$  and 0.0829  $\text{H}_2\text{O}$ .  $\text{C}=64.35$ ;  $\text{H}=4.79$ .

0.1997 „ 0.4716  $\text{CO}_2$  „ 0.0872  $\text{H}_2\text{O}$ .  $\text{C}=64.40$ ;  $\text{H}=4.82$ .

$\text{C}_{20}\text{H}_{18}\text{O}_7$  requires  $\text{C}=64.8$ ;  $\text{H}=4.81$  per cent.

A determination of the specific rotatory power of dibenzoylmannogalactan carried out in glacial acetic acid solution gave, as the mean of two observations,  $[\alpha]_D +23.0^\circ$

#### LÆVULOMANNAN.

The substance forming the reserve material of the ivory nut has been already investigated to some extent. Reiss (*Landwirthsch. Jahrbuch*, 1889, 18, 745) extracted the shavings of this nut with cold 75 per cent. sulphuric acid, and obtained a carbohydrate which he termed seminin. This substance swells up and partially dissolves in water; the solution is lævorotatory, and effects reduction of Fehling's solution. When hydrolysed with acids, seminose was formed, which E. Fischer subsequently (*Ber.*, 1889, 22, 1155) proved to be mannose. S. W. Johnson (*J. Amer. Chem. Soc.*, 1896, 18, 214) extracted ivory nut shavings with 10 per cent. caustic potash solution, and by precipitation with alcohol and subsequent purification, obtained a substance which had the composition  $\text{C}_6\text{H}_{10}\text{O}_5$ , and, on hydrolysis, yielded mannose.

In our examination of the ivory nut, the shavings, after treatment with cold 1 per cent. caustic alkali and subsequent washing with water, were boiled with 2 per cent. sulphuric acid for  $1\frac{1}{2}$  hours and filtered. The rather dark-coloured filtrate was neutralised, boiled with animal charcoal, filtered, and evaporated under diminished pressure to a syrup. This was then mixed with alcohol, and, as no crystalline sugar could be induced to separate, the syrup was dissolved in water, the alcohol removed, and an excess of phenylhydrazine acetate added. Immediately, a copious precipitate of mannose phenylhydrazone separated, which, some hours later, was collected, and the filtrate decomposed with benzaldehyde. In this way, it was found that, besides mannose, another sugar is produced on hydrolysing the carbohydrate of the ivory nut. It is lævorotatory, has a very sweet taste, gives phenylglucosazone (m. p.  $206^\circ$ ) when treated with phenylhydrazine acetate, and decomposes very readily with the separation of humous substances when boiled for a short time with hydrochloric acid. These reactions indicate the presence of lævulose, which was confirmed by the production of the characteristic claret-red coloration, and red precipitate when the solution, mixed with an





equal volume of concentrated hydrochloric acid, was carefully warmed with a small quantity of resorcinol dissolved in hydrochloric acid (Seliwanoff, *Ber.*, 1887, 20, 181; Hädicke and Tollens, *Zeits. Ver. Rubenzuckerind.*, 1891, 41, 895). Up to the present, however, we have not been successful in isolating the lævulose in a crystalline condition.

When the original syrup was oxidised by means of nitric acid, no mucic acid was obtained; and on distillation with hydrochloric acid, according to the directions of Flint and Tollens (*Ber.*, 1892, 25, 2912), less than 0·8 per cent. of furfuraldehyde was formed.

#### *Isolation of Lævulomannan.*

Ivory nut turnings were extracted in the cold with 5 per cent. aqueous caustic alkali. The extract was filtered through glass wool, and, to the clear filtrate, Fehling's solution, or cuprammonium hydroxide, was added until no further precipitation occurred. The voluminous blue copper compound was washed with water by decantation, then well kneaded and again washed with water. The washing must be conducted carefully, or, as in the case of manno-galactan, when the alkali is nearly all removed, the copper compound becomes soluble in water. The blue precipitate was next triturated with dilute hydrochloric acid, the resulting solution filtered and left for a few minutes, when a thick, white precipitate separated; this was collected and washed with water until free from acid. In this state, the substance dissolves easily in hot water, but on boiling the solution it separates completely in an insoluble form. Possibly, the substance in aqueous solution is in the state of a hydrate which, on boiling, becomes converted into an anhydride. The well-washed preparation was boiled with water for some time to completely convert the soluble modification into the insoluble form, which was collected, treated with hot alcohol, dried first in the air, then at 100°, and finally at 120°. It was only after repeated heating at the latter temperature and cooling in a vacuum that the whole of the moisture was removed; this behaviour resembles that of starch, which also requires prolonged heating at about 120° before it is completely dried.

When prepared in this manner, lævulomannan is a white, amorphous substance, soluble only in solutions of caustic alkalis. On analysis:

0·1893 gave 0·3058 CO<sub>2</sub> and 0·1046 H<sub>2</sub>O. C = 44·1; H = 6·11.

0·2031 „ 0·3279 CO<sub>2</sub> „ 0·1123 H<sub>2</sub>O. C = 44·0; H = 6·13.

C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> requires C = 44·4; H = 6·11 per cent.

Owing to the insolubility of this substance in water, the determinations of the rotatory power had to be made in caustic alkali solutions.

About 0.5 gram was boiled with a small quantity of water, cooled, and a few drops of strong aqueous caustic potash or soda added, any rise of temperature being avoided; the solution was made up to 25 c.c., filtered, and examined in a 100 mm. tube. The mean of six determinations from different preparations gave the value  $[\alpha]_D - 44.1^\circ$ .

### *Hydrolysis of Lævulomannan.*

About 0.5 gram of the substance was dissolved under the conditions mentioned above, 2 c.c. of concentrated hydrochloric acid were added, and the solution heated in a bath of boiling water for 15 minutes, cooled, made up to 25 c.c., filtered and examined at  $20^\circ$  in a 200 mm. tube. The mean specific rotatory power of the mixed sugars after inversion was  $[\alpha]_D + 9.5^\circ$  at  $20^\circ$ , the limits being within  $1^\circ$  of this value. Taking the value  $[\alpha]_D + 14.25^\circ$  for mannose, and  $[\alpha]_D - 88.7^\circ$  for lævulose,\* a mixture of 20 parts of mannose with 1 part of lævulose would have the rotatory power  $[\alpha]_D + 9.35^\circ$ , which closely approximates to the experimental value. We do not, however, wish to insist that on acid hydrolysis, lævulomannan yields a mixture of lævulose and mannose in the proportions just mentioned, as the lævulose is present in far too small a quantity to allow of accurate measurement.

Several estimations of mannose were made in the products of hydrolysis of lævulomannan by treating with phenylhydrazine acetate and weighing the phenylhydrazone formed. The following are the results obtained:

Inverted lævulomannan.	Mannose phenylhydrazone.	Mannose per cent.
0.3246	0.4276	87.9
0.9761	1.2990	88.7
0.3321	0.4945	89.3
0.3320	0.5045	91.1

The determinations were carried out with the object of estimating the mannose only approximately, and as no correction was made for the solubility of the phenylhydrazone in the mother liquors, the results are probably low; they serve, however, to establish the fact that lævulomannan yields at least 90 per cent. of mannose on hydrolysis as against 95 per cent. indicated by the rotatory power of the inverted solution.

*Dibenzoyllævulomannan*,  $C_6H_5O_5(CO \cdot C_6H_5)_2$ , prepared by acting on

\* According to Hönig, Schubert, and Jesser (*Wien. Akad. Ber.*, ii, 534 *Ber. Ref.*, 1887, 20, 721), the specific rotatory power of lævulose at  $20^\circ$  is expressed by the formula:  $[\alpha]_D = -113.9635^\circ + 0.2583 q$ , where  $q$  represents the percentage of water in the solution. In solutions of the inverted lævulomannan of the concentration employed by us,  $[\alpha]_D$  would therefore be about  $-88.7^\circ$ .

lævulomannan in alkaline solution with benzoyl chloride, was purified by solution in glacial acetic acid and precipitation with water, this treatment being thrice repeated. The substance is a white powder quite devoid of crystalline structure; it softens at 165—170°, and is soluble in benzene, alcohol, or glacial acetic acid. On analysis :

0.2349 gave 0.5803 CO<sub>2</sub> and 0.1048 H<sub>2</sub>O. C=64.9; H=4.70.

C<sub>20</sub>H<sub>18</sub>O<sub>7</sub> requires C=64.8. H=4.81 per cent.

Two determinations of the specific rotatory power in glacial acetic acid solution gave  $[\alpha]_D - 76.0^\circ$  as a mean value.

In conclusion, we wish to express our thanks to Mr. J. F. Briggs for having kindly supplied us with a quantity of the Indian clearing nut.

LABORATORY OF THE BEETROOT SUGAR ASSOCIATION.

## LIX.—*The Dissociation Constant of Azoimide (Hydrazoic Acid).*

By CHARLES ALFRED WEST, Assoc. R.C.S.

IN view of the remarkable properties of hydrazoic acid, it was thought that a determination of the avidity of the acid would be of interest. While the work was in progress, however, it was found that Ostwald had already determined the electrical conductivity of the acid and had ascertained that it was a somewhat stronger acid than acetic acid (compare Curtius, *J. pr. Chem.*, 1891, [ii], 43, 207). Professor Ostwald has been good enough to inform the author that the details of his work were never published and that they have not been preserved. In these circumstances, an account of the results obtained in the present experiments may be put on record.

### *Preparation of the Acid and Sodium Salt.*

The sodium salt of hydrazoic acid was prepared by the method described by W. Wislicenus (*Ber.*, 1892, 25, 2084). The product was dissolved in some of the water which had been prepared for the conductivity experiments, sulphuric acid added in slight excess, and the hydrazoic acid distilled off. Practically the whole had passed over when about one-third of the liquid had been distilled. The acid was estimated by titration with *N*/10 caustic soda, using phenolphthalein as indicator.

About 30 c.c. of the *N*/2 acid were neutralised with pure sodium hydroxide, then a little more of the acid was added, and the solution boiled for some time to expel the excess. The resulting solution was

not alkaline to phenolphthalein, but a drop placed on neutral litmus paper gradually, but very slowly, turned the litmus distinctly blue.

#### *Estimation of the Sodium Salt.*

As hydrazoic acid distils very readily, it was thought that the sodium salt might be estimated by adding excess of *N*/10 sulphuric acid, boiling off the hydrazoic acid and titrating the excess of sulphuric acid with soda.

This method of estimation was tested and found to be satisfactory by titrating a solution of hydrazoic acid with *N*/10 soda, adding excess of *N*/10 sulphuric acid, boiling for 20 minutes, and then titrating back with soda. The volumes of the soda and sulphuric acid solutions used were exactly equal, showing that all the hydrazoic acid had been expelled by boiling.

#### *Conductivity Experiments.*

The water used was prepared in a well ventilated laboratory, where no other work was going on, by distilling the laboratory distilled water first with sulphuric acid, then with baryta, and then alone. The water thus prepared had a conductivity of  $5.85 \times 10^{-6}$  Siemens' units. This was taken into account in the measurements below.

The conductivities were determined by Kohlrausch's method, by means of induction currents and a telephone. A covered cell with platinised platinum electrodes was used, the cell being immersed to within  $\frac{1}{4}$ th of an inch of the top in water at 25°.

To test the working of the apparatus, the conductivity of acetic acid was determined with the following results:

<i>v.</i>	Mol. conductivity found.	Mol. conductivity at 25° (Ostwald).
10	4.89	4.86
100	15.10	15.15
1000	45.3	45.6

The conductivity of sodium hydrazoate was then determined with the following results:

<i>v.</i>	$\mu$ .	<i>v.</i>	$\mu$ .
32	100.8	10	94.9
64	102.9	100	104.1
128	104.8	1000	108.2
256	105.5		
512	107.2		
1024	107.9		
2048	107.8		



$\mu_{\infty}$  will therefore have a value of about 109. The rate of increase in the conductivity of the *N*/100 solution of the sodium salt with increase in temperature was determined between 15° and 35°, and was found to be 2·7 per cent. per degree.

*Conductivity of Hydrazoic Acid.*

Taking  $\mu_{\infty} = 109$  for the sodium salt of hydrazoic acid, subtracting from this 44·5 for the velocity of the sodium ion, and adding 320·5 for hydrogen, we get 385 as the value of  $\mu_{\infty}$  for hydrazoic acid.

Measurements for the conductivity of hydrazoic acid were made with the following results:

<i>v.</i>	$\mu$ .	<i>m.</i>	<i>k.</i>
10	5·38	0·01397	0·0000198
100	15·98	0·0415	0·0000180
1000	45·97	0·1194	0·0000166

The value of *k* was also deduced from the rate of inversion of cane-sugar induced by the acid, and was found to be 0·0000186.

The dissociation of acetic acid in *N*/10 solution at 25° is 0·0133, and the value of *k* deduced from Ostwald's measurements is 0·0000180. The dissociation of hydrochloric acid in *N*/10 solution at 18° is 0·914. The avidity of hydrazoic acid is therefore a little greater than that of acetic acid, and only about one-seventieth of that of hydrochloric acid.

These determinations were carried out at the suggestion of Prof. Tilden, to whom the author is indebted for advice during the progress of the work.

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## LX.—*New Glucoside from Willow Bark.*

By HOOPER ALBERT DICKINSON JOWETT, D.Sc.

It has been generally assumed that the different species of willow bark contain the same glucoside—salicin—although in varying amount. Beck, for example (*Amer. J. Pharm.*, 1891, 63, 581), gives the results of the assay of different species of willow bark, but no proof that the same glucoside was obtained from all the varieties. Having had occasion to examine a bark purchased as black willow, I found that the crystalline principle obtained from it by the usual method for preparing salicin, was not that substance, but a new glucoside for

which the name of *salinigrin* is provisionally proposed. Unfortunately, it has not been possible to determine with certainty from what species of *Salix* the bark was obtained, for the identification of the different species of willow, even in living plants, is admitted by botanists to be a most difficult task. Beck (*loc. cit.*) gives the yield of salicin from *Salix nigra* as 0.73 per cent. The determination of the constitution of this new glucoside has revealed an extremely interesting fact, for whilst salicin is the glucoside of *o*-hydroxybenzyl alcohol, *salinigrin* is the glucoside of *m*-hydroxybenzaldehyde, a substance not met with hitherto in plants.

A proximate analysis of the bark showed that, in addition to *salinigrin*, it contains a large amount of tannin, colouring matter, and the ordinary plant constituents. The amount of extractive matter obtained by means of alcohol and of water was 8.5 and 9.5 per cent. respectively.

#### *Preparation of Salinigrin.*

The coarsely powdered bark was boiled with a convenient quantity of water for 2 hours, the decoction strained, and the marc pressed. The aqueous extract was then evaporated to a somewhat low bulk, 10 per cent. of lead acetate added, the mixture boiled for a few minutes, and set aside. It was then strained through calico, the excess of lead acetate removed by hydrogen sulphide, and the mixture filtered. It was finally neutralised with ammonia, evaporated to a low bulk, and set aside to crystallise. The crystals were then drained by the aid of the pump, recrystallised from hot water until white, and finally recrystallised from hot alcohol. The yield of purified glucoside was about 1 per cent. of the bark, or somewhat higher than the figure given by Beck for salicin.

#### *Properties of Salinigrin.*

The glucoside separates in needles or rosettes, which, however, coalesce during collection and draining; if crystallised from water, it forms a crystalline mass; better crystals can be obtained from alcohol. The purity of the product was determined by the fact that, after five crystallisations from water, once from acetone and from alcohol, the melting point was unchanged. The crystals are anhydrous and melt at 195° (corr.) without decomposition, solidifying to a crystalline mass on cooling. It is fairly soluble in cold, and exceedingly soluble in hot water, sparingly soluble in cold, but more so in hot alcohol, also sparingly soluble in hot acetone, and almost insoluble in ether, light petroleum, or chloroform. Determinations of its solubility in water and in alcohol gave the following results:

1. In water at 15°: 7.5220 solution gave 0.1412 salt, hence 1 part is soluble in 52.2 parts of water.

2. In alcohol at 15°: 4.9980 solution gave 0.0228 salt, hence 1 part is soluble in 218.2 parts of alcohol.

The glucoside is levorotatory, a determination of its specific rotation giving the following result:

$$\alpha_D = -3.5^\circ; l = 2 \text{ dm.}; c = 2.004; [\alpha]_D^{25} = -87.3^\circ.$$

Unlike salicin, it gives no colour reaction with sulphuric acid or with other reagents. It very slightly reduces Fehling's solution on boiling. On analysis, the following results were obtained:

0.255 gave 0.5178 CO<sub>2</sub> and 0.125 H<sub>2</sub>O. C = 55.37; H = 5.45.

0.2308 „ 0.4664 CO<sub>2</sub> „ 0.117 H<sub>2</sub>O. C = 55.11; H = 5.63.

C<sub>13</sub>H<sub>16</sub>O<sub>7</sub> requires C = 55.00; H = 5.63 per cent.

### *Hydrolysis of Salinigrin.*

When salinigrin is boiled with dilute acids, it undergoes hydrolysis, glucose and *m*-hydroxybenzaldehyde being formed. The hydrolysis is best carried out as follows: 2 grams are dissolved in 50 c.c. of 3 per cent. aqueous sulphuric acid, the liquid boiled in a reflux apparatus for 3 to 4 hours, and then set aside. On cooling, long, needle-shaped crystals separate, which may be filtered off. The acid liquid is then extracted three or four times with ether, the ethereal solution washed, dried, and distilled. The crystalline residue is then mixed with the crystals previously separated, and the product set aside for further examination.

In two experiments, the yield of the product soluble in ether was determined with the following results:

(1). 2 grams gave 0.9396 gram. Yield = 46.98 per cent.

(2). 4 „ „ 1.8294 „ „ = 45.74 „

Calculated for *m*-hydroxybenzaldehyde = 47.7 per cent.

The liquid, after extraction with ether, is warmed, and then neutralised with barium carbonate, filtered, and the neutral filtrate evaporated to a low bulk on the water-bath. On standing and further evaporation, a syrup is formed which gradually crystallises and becomes a solid mass,

### *A. Product Soluble in Ether.*

This, when first obtained, was slightly coloured and melted at 105°, but by recrystallising from water several times and decolorising with animal charcoal, long, needle-shaped crystals were obtained which, when dried at 100°, melted at 108° (corr.). The substance was only

slightly soluble in cold water, but freely so in alcohol, ether, chloroform, or benzene. The aqueous solution gave a violet coloration with ferric chloride and a precipitate with aqueous lead acetate solution. It also gave a precipitate with phenylhydrazine acetate and slightly reduced ammoniacal silver nitrate.

The air-dried crystals were found to contain  $\frac{3}{2}\text{H}_2\text{O}$ .

0.1506, at  $100^\circ$ , lost 0.0138  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 9.2$ .

$\text{C}_7\text{H}_6\text{O}_2 + \frac{3}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 9.9$  per cent.

The anhydrous compound was analysed with the following results :

0.137 gave 0.346  $\text{CO}_2$  and 0.063  $\text{H}_2\text{O}$ .  $\text{C} = 68.87$ ;  $\text{H} = 5.03$ .

0.1594 „ 0.4016  $\text{CO}_2$  „ 0.0748  $\text{H}_2\text{O}$ .  $\text{C} = 68.71$ ;  $\text{H} = 5.2$ .

$\text{C}_7\text{H}_6\text{O}_2$  requires  $\text{C} = 68.85$ ;  $\text{H} = 4.92$  per cent.

These properties agree exactly with those recorded for *m*-hydroxybenzaldehyde, with the exception of the water of crystallisation and the melting point, the latter being given as  $104^\circ$ , whilst the purified hydrolytic product melted at  $108^\circ$  (corr.). This small difference is probably due to increased purity, as when first crystallised the substance melted at  $105^\circ$ .

Further proof of the identity of the product with *m*-hydroxybenzaldehyde was furnished by the preparation of the following derivatives :

The *phenylhydrazone*, prepared by Clemm's method (*Ber.*, 1891, 24, 826), melted, when first obtained, at  $130^\circ$ , the temperature given by Clemm, but on recrystallisation from hot benzene, fused at  $147^\circ$  (corr.). It was more easily prepared by warming an aqueous solution of the aldehyde with phenylhydrazine dissolved in glacial acetic acid, and then melted at  $147^\circ$  (corr.). On analysis :

0.1494 gave 17 c.c. moist nitrogen at  $13^\circ$  and 759 mm.  $\text{N} = 13.43$ .

$\text{C}_{13}\text{H}_{12}\text{ON}_2$  requires  $\text{N} = 13.20$  per cent.

It would appear, therefore, that the melting point as given by Clemm is too low.

The *oxime* was prepared in the usual way and separated from benzene as an oil which slowly solidified. The crystalline mass melted at  $87-88^\circ$ , as described by Dollfuss (*Ber.*, 1892, 25, 1924). On recrystallising this mass from benzene, long, needle-shaped crystals were obtained, which, after several recrystallisations, melted at  $138^\circ$  (corr.), and were analysed with the following result :

0.048 gave 4.4 c.c. moist nitrogen at  $15^\circ$  and 755 mm.  $\text{N} = 10.63$ .

$\text{C}_7\text{H}_7\text{O}_2\text{N}$  requires  $\text{N} = 10.2$  per cent.

Whether the higher melting point is due to increased purity of the product or to change into a stereoisomeride was not determined.

The *2-nitro-m-hydroxybenzaldehyde*, which crystallised in yellowish-

brown needles melting sharply at  $128^{\circ}$  (corr.), as described by Tiemann and Ludwig (*Ber.*, 1882, 15, 2052), and the *m*-hydroxybenzoic acid, which melted at  $200^{\circ}$  (corr.), were also prepared for purposes of comparison.

### B. Identification of the Sugar.

The crystalline mass which was obtained by the hydrolysis was dissolved in hot methyl alcohol and filtered. On evaporation, it gave a few needle-shaped crystals, which could not be separated, and on further evaporation the syrup first formed solidified as before. It was therefore dissolved in water, digested with a little animal charcoal, and the filtrate slowly evaporated. The usual crystalline mass was obtained, and this, while still pasty, was placed on a porous plate to remove the mother liquor. The crystals were then powdered and dried in a vacuum over sulphuric acid. The sugar had no sharp melting point, and was dextrorotatory; a determination of its specific rotation, after the solution had stood for several days, gave the following result:

$$\alpha_D = +2.1^{\circ}; l = 1 \text{ dm.}; c = 4.14; [\alpha]_D = +50.7^{\circ}.$$

$$\text{For } d\text{-glucose, } \alpha_D = +52.7^{\circ}.$$

In the following qualitative reactions, the sugar behaved exactly like glucose; (i) it reduced Fehling's solution; (ii) with sodium *o*-nitrophenylpropionate, indigotin was obtained; (iii) with caustic soda, a reddish-brown coloration was produced; (iv) it gave the characteristic red colour with picric acid; and (v) charred only slowly with sulphuric acid.

Complete proof of its identity with *d*-glucose was furnished by the examination of the osazone. This was prepared in the usual way and was obtained in yellow crystals which melted at  $210^{\circ}$  (corr.) with decomposition. This is  $5^{\circ}$  higher than the melting point recorded for phenylglucosazone, but the melting points of this and of a specimen of phenylglucosazone, taken in the same bath, were found to be within one degree of each other. It has been pointed out (Beythien and Tollens, *Annalen*, 1889, 255, 217) that the melting points of osazones vary considerably, being dependent on the rate at which the bath is heated. The melting points just given were obtained by heating at an average rate. On analysis:

0.064 gave 0.1412  $\text{CO}_2$  and 0.0366  $\text{H}_2\text{O}$ .  $\text{C} = 60.17$ ;  $\text{H} = 6.34$ .

$\text{C}_{13}\text{H}_{22}\text{O}_4\text{N}_4$  requires  $\text{C} = 60.33$ ;  $\text{H} = 6.14$  per cent.

It is thus proved that salinigrin, on hydrolysis, yields quantitatively glucose and *m*-hydroxybenzaldehyde; its formula is therefore  $\text{C}_{13}\text{H}_{16}\text{O}_7$ . It can be easily distinguished from salicin by

affording with sulphuric acid a colourless solution, whilst salicin under similar conditions produces a blood-red colour. It would be possible to separate it from salicin by fractional crystallisation from alcohol, in which it is much the less soluble.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES.

## LXI.—*Bromination of Benzeneazophenol.*

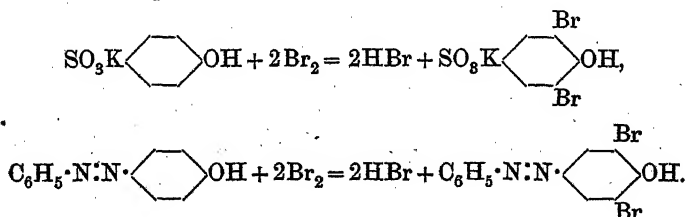
By J. T. HEWITT and W. G. ASTON.

RECENTLY, one of the authors of this communication (Trans., 1900, '77, 99) showed that when benzeneazophenol was nitrated with dilute nitric acid at a temperature of 40—45°, the dilution of the nitric acid being sufficient to preclude the formation of a salt from the acid and the azophenol in its tautomeric condition of quinonephenylhydrazone, one nitro-group entered into the ortho-position relatively to the hydroxyl group of the phenol nucleus, the substance behaving chemically as a true hydroxyl derivative of azobenzene. Such a reaction was hardly in accordance with Hantzsch's view that benzeneazophenol was a phenylhydrazone of quinone when in the free condition, and it was thought that the results so obtained formed at least as valid an argument for the phenolic formula as the contrary argument of Hantzsch, which, to a certain extent, was based on an incorrect determination of the dissociation constant for phenol (Hantzsch, *Ber.*, 1899, 32, 3069, 3082; Farmer and Hantzsch, *Ber.*, 1899, 32, 3089. Compare Walker, Trans., 1900, '77, 18; *Zeit. physikal. Chem.*, 1900, 32, 137).

Almost immediately after the appearance of this work, Professor Armstrong made a communication to the Society (Proc., 1899, 15, 243) in which he stated that although *p*-hydroxyazobenzene might be expected to be readily brominated in the ortho-position relatively to the hydroxyl group, it yields a product convertible into *p*-bromoaniline and phenol, and capable of being prepared from these substances, a result showing that towards bromine the substance brominated behaves as a hydrazone. Experiments on the bromination of benzeneazophenol had been undertaken in this laboratory last summer, but on account of the relative difficulty of regulating the reaction, were put aside until the nitration with dilute nitric acid had been studied and were resumed at once on the appearance of Prof. Armstrong's communication.\*

\* I received letters from Prof. Meldola and Prof. Auwers soon after the publication of Prof. Armstrong's note. Prof. Meldola told me that he had some few years

We found that when benzeneazophenol was dissolved in acetic acid, and sodium acetate added to prevent any liberation of hydrogen bromide—which as a strong mineral acid forms a salt of quinone phenylhydrazone—the first product of bromination was benzeneazo-*o*-dibromophenol, and not a monobromo-derivative. The reaction is, in fact, the complete analogue of that between potassium phenol-*p*-sulphonate and bromine; in the latter case, Senhofer (*Annalen*, 1870, 156, 103), when he used molecular proportions of the reacting compounds, obtained a mixture of unaltered substance and its dibromo-derivative. The two reactions may be represented by the similar equations,



At the risk of giving too much, rather than too little detail, we describe first the reaction when molecular proportions are employed, and afterwards the process adopted for obtaining benzeneazodibromophenol in quantity. Five grams of benzeneazophenol and 10 grams of crystallised sodium acetate were dissolved in 50 grams of hot glacial acetic acid, the solution was then cooled down to the ordinary temperature and violently agitated in a conical flask, whilst 4 grams of bromine in 20 grams of glacial acetic acid were run in drop by drop. The addition took 10 to 15 minutes, and at the end of the operation the temperature was 26°. After standing a further 10 minutes, the contents of the flask were poured into cold water, collected, washed, and distilled with steam; 0.02 gram of tribromophenol (m. p. 95°) separated from the aqueous distillate (about 600 c.c.). The residue in the flask was collected and fractionally recrystallised from glacial acetic acid. The first crop of crystals was twice recrystallised from

ago brominated benzeneazophenol in glacial acetic acid solution, adding sodium acetate. Under these conditions, he obtained an oily substance which he regarded as benzeneazo-*o*-bromophenol; he also recommended me to use sodium acetate to bind free hydrogen bromide, and very kindly left the rest of the work in my hands. I wish to tender my best thanks to Prof. Meldola for his kindness and advice, and to Prof. Auwers who had also undertaken the bromination of benzeneazophenol, but abandoned it on the appearance of the papers by Prof. Armstrong and myself. Prof. Auwers considered that it was very probable that Prof. Armstrong had been brominating a salt of quinonephenylhydrazone, as he had himself noticed that the first drop of bromine in a glacial acetic acid solution of benzeneazophenol produced a carmine-red precipitate.—J. T. HEWITT.

glacial acetic acid, and when washed and dried weighed 1.55 grams ; it melted at  $135^{\circ}$  (corr.). On analysis :

0.1102 gram gave 7.80 c.c. moist nitrogen at  $18^{\circ}$  and 746 mm.  $N = 8.02$ .

$C_{12}H_8ON_2Br_2$  requires  $N = 7.88$  per cent.

From the united mother liquors, a second crop of crystals (0.56 gram), melting at about  $127^{\circ}$  (uncorr.), was obtained, and by successive additions of water two further crops, the first (0.59 gram) a mixture with a melting point of about  $80^{\circ}$ , the second (2.30 grams) consisting essentially of benzeneazophenol.

The identity of the purified first crop with benzeneazodibromophenol was proved by adding a diazotised solution of aniline to an alkaline solution of 2:6-dibromophenol, and allowing this to stand overnight. On the addition of hydrochloric acid, a tarry mass separated ; steam was blown through to remove unaltered dibromophenol, and the tarry residue repeatedly recrystallised from dilute spirit. This left most of the tar undissolved, and by stirring the solution as it cooled, orange needles were deposited. After several such recrystallisations, the substance was found to have the same melting point as the product obtained by the direct bromination of benzeneazophenol, and a mixture of the two preparations dissolved in benzene and evaporated also melted at the same temperature.

It may be mentioned that the yield of substance obtained in coupling phenyldiazonium chloride with alkaline dibromophenol is extremely small, most of the dibromophenol being recovered unchanged.

The process finally adopted in the preparation of benzeneazodibromophenol is to dissolve recrystallised benzeneazophenol (25 grams), together with its own weight of fused sodium acetate in 10 times its weight of glacial acetic acid (250 grams), then, after cooling below  $10^{\circ}$ , to run in, drop by drop, 32 grams of bromine, dissolved in 100 grams of glacial acetic acid, agitating vigorously the whole time, and taking care that the temperature does not rise. During the addition of the bromine, the substance separates out as yellow crystals ; to render the separation as complete as possible, final cooling to  $0^{\circ}$  is desirable, and in this way 27 grams of the dry product having the correct melting point were obtained. From the mother liquors, a further quantity of a slightly less pure substance may be recovered, making the total yield nearly quantitative. A great advantage of the process is that the acetic acid is neither diluted nor contaminated with hydrogen bromide, so that it is easily recovered by distillation. On recrystallisation of the benzeneazodibromophenol from benzene, it is obtained in beautiful, long, orange needles, which melt at  $136^{\circ}$  (corr.). On analysis :



0.1271 gave 0.1943  $\text{CO}_2$  and 0.0253  $\text{H}_2\text{O}$ .  $\text{C} = 41.12$ ;  $\text{H} = 2.21$ .

0.1751 „ 11.8 c.c. moist nitrogen at  $10^\circ$  and 760 mm.  $\text{N} = 8.07$ .

0.1989 „ 0.2109  $\text{AgBr}$ .  $\text{Br} = 45.12$ .

$\text{C}_{12}\text{H}_8\text{ON}_2\text{Br}_2$  requires  $\text{C} = 40.44$ ;  $\text{H} = 2.27$ ;  $\text{N} = 7.88$ ;  $\text{Br} = 44.91$  percent.

Benzeneazo-*o*-dibromophenol is very soluble in acetone, and easily soluble in hot benzene, chloroform, ether, or ethyl acetate; glacial acetic acid and "methylated" spirit dissolve it sparingly in the cold, whilst it is nearly insoluble in light petroleum.

A benzene solution of benzeneazodibromophenol, although darkened in colour by hydrogen chloride, is not precipitated; if, however, the substance is intimately ground with strong sulphuric acid, a carmine-red mass, evidently a sulphate, is obtained. On treating this sulphate with water, it becomes yellow, forming a crystalline powder which, after drying in the air, has the melting point  $134^\circ$  (uncorr.). A hydrate had evidently not been produced by the treatment.

Hot caustic soda solution readily dissolves the azophenol, and a sodium salt separates in fine yellow needles on cooling. After drying at  $110^\circ$  until of constant weight, the compound was analysed:

0.2707 gave 0.0491  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 5.88$ .

$\text{C}_{12}\text{H}_7\text{ON}_2\text{Br}_2\text{Na}$  requires  $\text{Na} = 6.08$  per cent.

An aqueous solution of this salt gives precipitates with salts of the heavy metals; it is noticeable that the barium salt is soluble in boiling water, and separates in yellow needles on cooling. This behaviour contrasts with that of barium benzeneazo-*o*-nitrophenolate which forms a nearly insoluble vermilion precipitate; the difference is perhaps due to the structure of the nitro-group.

The *acetyl* derivative, obtained by heating the phenol for 2 hours with 3 to 4 times its weight of acetic anhydride, crystallised from glacial acetic acid in yellow needles and melted at  $143^\circ$ .

0.1584 gave 0.1496  $\text{AgBr}$ .  $\text{Br} = 40.16$ .

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\text{Br}_2$  requires  $\text{Br} = 40.17$  per cent.

The substance dissolved easily in acetone or chloroform, and moderately easily in benzene, ether, or ethyl acetate, but only sparingly in the other common organic solvents.

The *benzoyl* derivative, prepared by boiling benzeneazodibromophenol with 3 to 5 times its weight of benzoyl chloride for 20 to 30 minutes, crystallises from hot spirit in beautiful, orange leaflets melting at  $120^\circ$  (corr.). The only solvents which dissolve this substance at all easily in the cold are acetone, benzene, ether, and ethyl acetate; it requires about 50 times its weight of boiling spirit, or over 200 times its weight of cold spirit, for solution.

0.1310 gave 7.1 c.c. moist nitrogen at  $18^\circ$  and 746 mm.  $\text{N} = 6.14$ .

$\text{C}_{19}\text{H}_{12}\text{O}_2\text{N}_2\text{Br}_2$  requires  $\text{N} = 6.11$  per cent.

*Ethyl Ether*.—None of the other derivatives prepared showing any instability of the bromine atoms, the examination of the ethyl derivative promised especial interest on account of Prof. Armstrong's statement that benzeneazo-*o*-bromophenetole easily loses bromine when dissolved in acetone. The ethyl ether was prepared by adding a mixture of 2 grams of ethyl bromide and 3 grams of absolute alcohol to 3 grams of the sharply dried and finely powdered sodium salt contained in a small bottle. This was tightly corked and shaken, the salt dissolved at once, and almost immediately small crystals of sodium bromide began to make their appearance. The reaction was completed by heating for 45 minutes to 100°; after cooling, the contents of the bottle were poured into warm dilute caustic soda, the oil which separated subsequently solidifying. The substance was washed repeatedly, and finally recrystallised from dilute spirit, silky, yellowish-orange needles melting at 71° (corr.) being obtained.

0.1215 gave 7.80 c.c. moist nitrogen at 12° and 752 mm.  $N = 7.54$ .

$C_{14}H_{12}ON_2Br_2$  requires  $N = 7.31$  per cent.

This ethyl ether is dissolved easily by most organic solvents, especially by acetone and ether; it is, however, only sparingly soluble in light petroleum.

From Prof. Armstrong's statement, it might be expected that this substance would react with acetone; in fact, with bromine atoms on either side of the ethoxyl group, an even greater reactivity might be expected than in the case of benzeneazo-*o*-bromophenetole. After boiling for 1 hour with acetone and then evaporating the solvent, no smell of bromoacetone was detected; the residue—which crystallised beautifully—was found to contain bromine, to melt at the original temperature, and when mixed with a portion of the analysed sample, which had not been treated in this manner, to be without influence on its melting point. The only conclusion to be drawn is that benzeneazodibromophenetole is unchanged by acetone under the conditions mentioned.

Although, when a substance exhibits tautomerism, it is only natural to expect that both configurations will be represented in any specimen, the vastly preponderating quantity of benzeneazophenol consists of the phenolic modification, both bromination and nitration experiments leading to the same conclusion. The results thus obtained coincide with those deduced from physical measurements by Auwers. Further experiments are in progress in this laboratory, the results so far obtained confirming those already published.

EAST LONDON TECHNICAL COLLEGE.

## LXII.—*Decomposition of Chlorates. Part II. Lead Chlorate.*

By WILLIAM H. SODEAU, B.Sc.

LEAD chlorate was prepared by adding carefully purified lead carbonate in excess to chloric acid, and on the following day slowly heating to the boiling point before filtering. The crystals obtained by concentrating the filtrate gave only a very faint opalescence with silver nitrate. They dissolve in about one-third of their weight of water at 19°, but do not deliquesce\* unless the air is practically saturated with moisture. Commercial lead chlorate was found to contain barium which could not be removed by fractional crystallisation. It was noticed that mixed crystals were deposited when a saturated solution of barium chlorate was added to one of lead chlorate.

The crystallised lead chlorate was heated at about 140° under reduced pressure until apparently dehydrated, the mass was then finely powdered and heated at 130—140° under 3 mm. pressure for 50 minutes. The white, anhydrous product was neutral to methyl-orange; the minute trace of chloride had not increased.

### *Examination of the Products of Decomposition.*

A standard solution was prepared by dissolving barium peroxide in excess of nitric acid and diluting until it exactly neutralised an equal volume of decinormal alkali; this solution kept fairly well in the dark and readily dissolved lead peroxide. The amount of oxide left, and consequently the amount of chlorine evolved, was ascertained by dissolving the residue in a known volume of this solution and titrating back with *N*/10 soda; methyl-orange worked well in the absence of unaltered chlorate, but the turbidity produced by a very slight excess of soda afforded an end reaction, which was preferred. The lead chloride was determined in the same portion by adding nitric acid and titrating with *N*/10 silver nitrate. The numerical results (including the weight of chlorate actually decomposed) given in this paper were calculated from analyses, but when practicable the gas was passed through potassium iodide solution; the latter did not become alkaline, and the amount of liberated iodine agreed with that of the oxide found in the residue, hence the gas must have been practically free from ozone and from oxides of chlorine.

\* Wächter (*J. pr. Chem.*, 1843, 30, 329) states that  $\text{Pb}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  is not deliquescent, but this has been misquoted in more than one treatise.

In residues free from undecomposed chlorate, but not overheated, the amount of oxygen, found by difference, was practically that required to form peroxide; portions washed free from chloride were but little affected by boiling dilute nitric acid. A small quantity of lower oxide is apt to be formed by local overheating, owing to rapid decomposition.

The loss of weight during incomplete decomposition agreed fairly well with that calculated by subtracting the weights of peroxide and chloride, as found by titration, from the equivalent amount of lead chlorate; formation of perchlorate would have led to a smaller loss of weight, and so must have been very slight, as might be expected from the weakness of the base. Some residues free from chlorate were mixed together and portions reheated in oxygen until the 52.4 per cent. of peroxide had entirely decomposed, leaving a cream coloured mass; only minute traces of chlorine were evolved (requiring, for example, 0.2 c.c. *N*/100 thiosulphate per gram) and the redetermination of oxide indicated no increase, although the temperature had reached 450°. Other portions were heated in chlorine; 18.4 per cent. of the peroxide present was converted into chloride in 10 minutes at about 200°, but at about 240° the action was even more marked, 30.9 per cent. being converted in the same period. These are approximately the average temperatures employed in the decompositions under 760 mm. and 4 mm. pressure respectively, hence much of the chlorine evolved must be reabsorbed unless special precautions are taken.

It is thus seen that lead chlorate decomposes into lead chloride, oxygen, lead peroxide, and chlorine, the last two being the only products tending to react with each other under the conditions of a slow decomposition of the chlorate.

#### *Slow Decomposition.*

For studying slow decomposition under various pressures, the substance was placed in a soft glass tube closed at one end, 12—18 mm. bore, and about 20 cm. in length. By means of an india-rubber stopper, the tube was connected to a T-piece, one limb of which communicated with a vacuum gauge filled with strong sulphuric acid, the pressure under which the decomposition actually took place being shown on a scale in terms of mm. of mercury, whilst the other limb led to the absorption tubes containing either aqueous potassium iodide (for pressures greater than 15 mm.), or else undried granular soda-lime followed by glass beads covered with a solution of potassium iodide in glycerol as a test for unabsorbed chlorine. The last absorption tube was connected to a delivery tube, either directly or through a Fleuss pump, in order that the progress of the decomposition might be followed by noting the volume of the oxygen evolved. Some anhy-

drous lead chlorate (usually 1 gram) having been weighed into the tube, the lower end was covered with soot, and placed in a bath of fusible metal provided with a thermometer (readings corrected for exposed column). Before decomposition commenced, any trace of absorbed moisture was removed by heating under reduced pressure at about  $160^{\circ}$  for some time, dry air being admitted through a side branch, and then pumped out. At the conclusion of the experiment, the gaseous contents of the tube were removed by repeated exhaustion and admission of air, and the residue then weighed and analysed as already described. The substance did not fuse unless the decomposition chanced to become rapid; the tubes were not corroded, and remained fairly constant in weight. The experiments have been numbered in the order in which they were performed, and to facilitate comparisons, the chlorine has always been stated per 100 parts contained in the weight of chlorate actually decomposed. It will be seen from Table I that the proportion of chlorine remaining free varied greatly with the conditions. Six decompositions, namely, those numbered 70b and 70a; 71b and 71a; 73b and 73a, were performed in pairs as indicated, two tubes being placed together in the bath, the first of the pair being under atmospheric pressure, and the other under 20—25 mm.; in experiments 70b, 71b, and 73b, the gas in the tube remained in contact with the residue until the companion decomposition was complete; this permitted further reabsorption (p. 718), and these decompositions gave less chlorine (46.3 per cent.) than did experiment 77 (53.3 per cent.). The reabsorption was most marked towards the end of the decomposition, for the temperature had then been increased, and much peroxide was present; incomplete decomposition gave more free chlorine, amounting to 60.6 per cent. in experiment 92.

Reduction of pressure greatly decreased the reabsorption, especially when decomposition was not completed; the most successful experiments gave: At 4 mm., 79.1 per cent. of chlorine free and 20.9 per cent. as chloride; at 1 to 2 mm., 81.4 per cent. free and 18.6 per cent. as chloride. At pressures below 4 mm., some chlorine reached the pump, perhaps owing to the removal of moisture from the soda-lime.

Lead chlorate was intimately ground up with half a molecular proportion of lead chloride; the absorbed moisture caused the mixture to cake when re-dried before partially decomposing in the manner just described. Deducting the added chloride, the residue at 4 mm. contained 20.9 per cent. of the possible chloride, whilst at atmospheric pressure the percentage was 43.6; these are about the usual proportions, hence little or no chlorine was expelled from the chloride during the decomposition. Addition of chloride does not appear to influence the ease of decomposition.

As in the case of barium chlorate (Trans., 1900, 77, 139), the use

of a bath of constant temperature was impracticable; the range was about  $190-210^{\circ}$  at atmospheric pressure, but a temperature of  $225-260^{\circ}$  was required for the somewhat slower decompositions under 4 mm., although  $225^{\circ}$  soon caused violent decomposition under atmospheric pressure. In some experiments, a second thermometer was placed inside the decomposition tube, so that its bulb was completely surrounded by chlorate; the temperatures thus indicated during decomposition at atmospheric pressure were slightly above those of the bath, and about  $30^{\circ}$  lower than those at 4 mm.; toward the end of the decompositions, the difference was even greater. It is thus seen that the temperature of the substance must be increased in order to compensate for the *impeding* effect of reduction of pressure.

To prevent the reabsorption of chlorine, it is necessary to decrease the concentration without increasing the temperature; this was accomplished by employing a stream of dry nitrogen at atmospheric pressure, frequent titrations of the liberated iodine affording guidance in heating the bath.

In the first series (Nos. 120—134, Table II.), the nitrogen was passed through the chlorate by means of a narrow tube reaching nearly to the bottom of one of the decomposition tubes previously employed, to which a side tube had been added as an exit for the gases. In this series, the smallest proportion of chloride was 14.5 per cent. (hence free chlorine = 85.5 per cent.), using 1.8 litres of nitrogen for 1 gram of chlorate; a larger current blew a large channel through the mass, and the cooling effect on the surface necessitated overheating of the exterior portions. The simultaneous employment of reduced pressure failed from similar causes.

In the second series (Nos. 137—140), there was less surface cooling; two U-tubes, each of 7 mm. bore and containing 0.5 gram of chlorate, were placed side by side, deep in the bath, and connected in series so that the chlorine evolved from one portion was carried over the other. It will be seen from Table II that the residues in the two tubes approached each other in composition as the current of nitrogen was increased; thus, with 0.9, 1.2, 4 and 5 litres, the differences were 5.9, 5.5, 0.3 and 0.1 per cent. respectively. With the larger volumes of nitrogen, the chlorine from the first tube can have had practically no effect upon the contents of the second, hence it seems fair to conclude that the reabsorption of chlorine had been all but eliminated, and that about 12.5 per cent. of the possible chloride is formed directly in the decomposition, about 87.5 per cent. of the total chlorine being liberated.

*Rapid Decomposition.*

An attempt has been made to ascertain the amount of chlorine at first liberated when lead chlorate is rapidly heated, the mass then becoming incandescent in places and much of the peroxide being decomposed by the heat, which, of course, promotes reabsorption of chlorine. The rapid decompositions were conducted in much the same way as the first of the slow decompositions already described. In experiments 74 and 75 (Table I), the greater part of the substance decomposed in about three seconds on the bath reaching a temperature of about  $225^{\circ}$ , but the heating was continued until the last traces had been decomposed; in experiment 76, the residue was heated until converted into oxychloride. The amounts of chlorine remaining free were respectively 45.5, 47.3, and 32.9 per cent. of the total in the chlorate; the last result confirmed Wächter's statement (*J. pr. Chem.*, 1843, 30, 329) that the oxychloride has the composition  $\text{PbO}, 2\text{PbCl}_2$ .

In the subsequent experiments, the bath was rapidly heated and the decomposition semi-explosive, most of the gas being evolved in about one second. Experiments 95 and 96 (Table I) commenced at atmospheric pressure, and the free chlorine amounted to only 38.1 and 39.0 per cent. in these, although the gas was removed as soon as possible after the rush had taken place. The thermometer bulb had acquired a temperature of about  $235^{\circ}$  at the moment of decomposition. With semi-explosive decomposition under reduced pressure, the apparatus was several times modified in order to avoid a marked rise of pressure; the following arrangement was finally employed. The upper end of the decomposition tube, 18 mm. in diameter, was sheathed with india-rubber tubing and inserted in the neck of an inverted "Winchester quart" bottle, constriction being thus avoided; a short side branch was connected to a double T-piece leading to the manometer, a Fleuss pump, and a stoneware bottle of 20 litres capacity. The whole was exhausted to 6 mm., and, immediately the rush of gas had taken place, the bath was removed and dry air admitted through an inlet near the bottom of the decomposition tube in order to remove chlorine. Each improvement gave a lower maximum pressure and a larger proportion of free chlorine; in the last experiment, the maximum pressure in the tube could not have greatly exceeded the 16 mm. recorded; 58.7 per cent. of the chlorine remained free, but there was no real indication of a limit. The thermometer reading was about  $270^{\circ}$  at the moment of decomposition.

A current of nitrogen did not prove useful in the case of these rapid decompositions.

TABLE I.—*Lead chlorate decomposed under various pressures.*

No.	Duration.	Proportion decomposed (per cent.).	Pressure.	Chlorine (total in decomposed portion=100).		Mols. chloride. Mols. oxide.
				Free.	As chloride.	
74	About 8 sec.	Nearly 100	1 atmosphere	45.5	54.5	1.21
75	" "	" "	"	47.3	52.7	1.11
76	" "	" "	"	32.9*	67.1	2.10
95	About 1 sec.	" "	"	38.1	61.9	1.62
96	" "	" "	"	39.0	61.0	1.56
100	" "	" "	6-->200 mm.	46.8	53.2	1.13
101	" "	" "	" "	48.4	51.6	1.06
102	" "	" "	6—170 "	54.5	45.5	0.837
103	" "	" "	" "	54.4	45.6	0.838
106	" "	" "	6—20 "	58.6	41.4	0.707
107	" "	" "	" "	58.4	41.6	0.712
118	" "	" "	" "	58.0	42.0	0.723
119	" "	" "	6—16 "	58.7	41.3	0.703
70b	35 min.	100	1 atmosphere	47.5†	52.5	1.10
71b	25 "	"	"	46.0†	54.0	1.18
73b	40 "	"	"	45.3†	54.7	1.21
77	65 "	"	"	53.3	46.7	0.88
85	15 "	28.1	"	59.4‡	40.6	0.684
92	27 "	61.6	"	60.6	39.4	0.650
70a	90 "	100	20—25 mm.	75.1	24.9	0.382
71a	80 "	"	" "	76.3	23.7	0.311
73a	110 "	"	" "	74.6	25.4	0.342
86	30 "	62.5	6 mm.	77.6	22.4	0.290
87	25 "	63.8	4 "	79.1	20.9	0.265
88	25 "	63.8	" "	78.8	21.2	0.269
89	23 "	65.4	" "	76.8	23.2	0.301
81	110 "	86.4	1—2 mm.	81.4	18.6	0.238

\* Heating continued until all peroxide had decomposed.

† Gas remained in contact with residue for some time.

‡ 3 grams decomposed in narrow tube.

The average range of the temperature of the bath was about 190—210° in the slow decompositions at atmospheric pressure, and 225—260° in those at 4 mm.



TABLE II.—*Lead chlorate decomposed in a stream of nitrogen.*

No.	Duration. (minutes).	Proportion decomposed. (per cent.).	Litres of nitrogen. (N.T.P.)	Chlorine (total in decomposed portion=100).		Mols. chloride. Mols. oxide.
				Free.	As chloride.	
120	22	69.0	1.1	84.3	15.7	0.187
121	12	78.7	1.8	85.5	14.5	0.167
124	20	78.0	5.4	75.4	25.6	0.344
125	40	81.8	5.9	77.9	22.1	0.284
126	20	about 80	1.1	79.8	20.2	0.254
131	15	65.5	0.5	75.7	24.3	0.321
132	13	40.6	0.5	78.4	21.6	0.276
133	17	36.2	0.6	79.9	20.1	0.252
134	40	39.8	1.0*	80.6	19.6	0.243
127	25	88.2	0.8*	84.8	15.2	0.180
<hr/>						
137	50	{ a 73.9 b 94.1 }	0.9	{ 84.3 78.4 }	{ 15.7 21.6 }	{ 0.187 0.276 }
138	50	{ a 61.2 b 73.0 }	1.2	{ 87.1 81.6 }	{ 12.9 18.4 }	{ 0.148 0.225 }
139	85	{ a 44.2 b 86.5 }	5.0	{ 86.7 86.6 }	{ 13.3 13.4 }	{ 0.154 0.155 }
140	76	{ a 58.4 b 75.8 }	4.0	{ 87.5 87.2 }	{ 12.5 12.8 }	{ 0.143 0.147 }

\* For 0.5 gram of chlorate.

In experiments 137—140, a=first U-tube, b=second U-tube; each contained 0.5 gram chlorate.

### Conclusions.

*Slow Decomposition.*—The mode of discussion adopted in the case of barium chlorate (Trans., 1900, 77, 147) is applicable to the results given in the present paper, and the latter appear to furnish an experimental confirmation of some of the reasoning employed in Part I, (*loc. cit.*). Lead chloride does not lose chlorine during the decomposition of lead chlorate mixed with it, or even when heated at 450° with lead peroxide in a stream of oxygen. These results show that chlorine and oxide must be direct products of decomposition and are not derived from lead chloride as supposed by H. Schulze (*J. pr. Chem.*, 1880, [ii], 21, 424). Decomposition under reduced pressure requires the employment of a *higher* temperature and is hence not quite satisfactory as a means of eliminating the secondary reaction between chlorine and lead peroxide, as this is greatly accelerated by rise of temperature; thus, 81.4 per cent. of the total chlorine remained free

under 2 mm., as compared with 45.3 to 60.6 per cent. under atmospheric pressure, but the employment of a stream of dry nitrogen gave results indicating 87.5 per cent. as the limit when reabsorption of chlorine is completely eliminated. About 12.5 per cent. of the total possible chloride must therefore be formed directly; this excludes Spring and Prost's theory that the whole of the chloride is formed by the action of chlorine on the oxide (*Bull. Soc. Chim.*, 1889, [iii], 1, 340).

The numerical results for the first action of heat might be expressed by the equation:  $8\text{Pb}(\text{ClO}_3)_2 = 7\text{PbO}_2 + \text{PbCl}_2 + 4\text{Cl}_2 + 17\text{O}_2$ , but unless an equation is employed including the terms  $\text{BaO} + 1500\text{BaCl}_2$  to express the decomposition of barium chlorate (*loc. cit.*) it seems better to regard the decomposition as consisting of two independent reactions, namely,  $\text{Pb}(\text{ClO}_3)_2 = \text{PbCl}_2 + 3\text{O}_2$  and  $\text{Pb}(\text{ClO}_3)_2 = \text{PbO}_2 + \text{Cl}_2 + 2\text{O}_2$ , the latter proceeding at about seven times the rate of the former. In the case of this chlorate, there is a marked secondary reaction,  $\text{PbO}_2 + \text{Cl}_2 = \text{PbCl}_2 + \text{O}_2$ , occurring to an extent depending upon the conditions and sometimes involving most of the chlorine first liberated; Spring and Prost (*loc. cit.*), working with large quantities, obtained only 8 per cent. of the total chlorine instead of 87.5 per cent.

It is difficult to decide whether the peroxide is formed directly or by oxidation of the monoxide, but it seems probable that its occurrence may be intimately connected with the practical absence of perchlorate, as the tendency to form perchlorate would appear to be the cause of the reducing properties of heated potassium chlorate (Fowler and Grant, *Trans.*, 1890, 57, 282).

*Rapid Decomposition.*—If the substance is made to decompose in about one second, the high temperature, resulting from the reaction, causes the formation of oxychloride and prevents the successful elimination of the reabsorption of chlorine. At atmospheric pressure, 38.5 per cent.\* of the total chlorine was obtained and this was increased step by step to 58.5 per cent. at 6—20 mm. without any indication of finality. The increase seems comparable with that similarly obtained in complete slow decomposition (53 per cent. at atmospheric pressure, and 75 per cent. at 20—25 mm.), so the results would not seem to prove that less chlorine was evolved during rapid decomposition. It seems probable that the decrease in the amount *remaining* free is due to the high temperature causing very active reabsorption rather than an alteration in the proportion first evolved. If the decomposition into peroxide, chlorine, and oxygen were endothermic, an increase of chlorine with rise of temperature would be expected, but the thermochemical aspect cannot well be discussed until the heat of formation

\* Further decreased when the gas was not removed immediately (see expt. 76, Table I).

of lead chlorate has been determined, as the difference between chloride and peroxide is neither large enough nor small enough to warrant a conjecture.

It may be noted that this *decrease* in the proportion of chlorine remaining free appears to invalidate the mode of reasoning adopted by Spring and Prost (*loc. cit.*) in deducing their theory partly from the increase observed in the case of certain chlorates, but supports the author's criticism of their reasoning (Trans., 1900, 77, 147). Barium chlorate showed no reabsorption, but there was a marked increase of free chlorine with rapid decomposition, whilst lead chlorate showed marked reabsorption but no increase; in these cases, the supposed cause and effect do not occur together.

It seems probable that the conclusions deduced in the case of slow decomposition (p. 724) will apply to rapid decomposition with but little modification, the main difference being that in the latter case the high temperature decomposes some of the peroxide (giving oxychloride) and causes the reabsorption of chlorine to be more marked.

The author desires to record his thanks for the advantages afforded him at the Davy-Faraday Research Laboratory whilst carrying out the earlier portions of this work, which has been continued at the Royal Agricultural College, Cirencester.

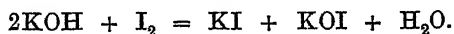
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### LXIII.—*Action of Iodine on Alkalis.*

By ROBERT LLEWELLYN TAYLOR.

IN a paper recently published on this subject by E. Péchard (*Compt. rend.*, 1899, 128, 1453), the conclusions arrived at are so remarkably at variance with the results of other experimenters that it seemed to me desirable to make some attempt to clear up this much disputed point. In a former paper on hypiodous acid and hypiodites (*Memoirs of Lit. Phil. Society, Manchester*, 1897, 41, 8, and *Chem. News*, 1897, 76, 17, 27), an account was given of experiments which I had made, confirming and extending Schönbein's original observations on this subject. In those experiments, I used an aqueous solution of iodine, and various alkalis. In order to ascertain the amount of hypiodite produced, I employed a method first described by Schwicker (*Zeit. physikal. Chem.*, 1895, 16, 303), wherein advantage is taken of the fact that a mixture of hypiodite and iodide is completely decomposed by carbonic acid, or even by an acid carbonate, with liberation of iodine, whereas a mixture of iodide and iodate is not so decomposed. I

showed that when an alkali is added to aqueous iodine, and a little ordinary soda-water, or potassium or sodium hydrogen carbonate immediately added, from 95 to 97 per cent. of the iodine originally used is liberated, showing that practically the whole of the iodine had undergone the reaction represented by the equation :



The hypoiodite in these dilute solutions decomposed, slowly at the ordinary temperature, but rapidly on heating, into iodate and iodide :



As originally pointed out by Lenssen and Löwenthal, the reaction between iodine and alkalis is a balanced one, and may be represented thus :



Consequently, the amount of alkali required to complete the reaction is considerably more than the theoretical.

Péchar'd (*loc. cit.*) describes how he attempted to ascertain the amounts of free iodine, iodide, iodate, and hypoiodite in solutions produced by adding iodine to alkalis, employing an elaborate series of determinations of total iodine, iodine as hypoiodite, and iodine as iodate. The whole series of operations must have taken a considerable time (and with such unstable solutions this is of great importance), and it is therefore not surprising that Péchar'd's results were not very definite. One of his results appears to have been that the amount of hypoiodite formed is proportional to the amount of alkali used, and another that the *iodate* formed amounts to 92 per cent. of the iodine used when a certain amount of alkali was employed. These remarkable conclusions led me to make the further experiments which are now described.

In the earlier investigation, I confined myself to an aqueous solution of iodine, but, as Péchar'd's experiments were made with iodine dissolved in an iodide, I decided to use similar solutions. I satisfied myself once more that Schwicker's method of estimating the amount of a hypoiodite is perfectly trustworthy—that is, carbonic acid or an acid carbonate has no action on a mixture of iodide and iodate. All that is needed, therefore, to estimate the amount of hypoiodite in a solution, if, as is practically always the case, there is also an iodide present, is to add a considerable excess of sodium hydrogen carbonate and a little soda-water, and then to estimate the liberated iodine by means of a standard solution of arsenious acid.

The solution of iodine generally used was of decinormal strength—about sixty times as strong as the aqueous solution I had formerly employed—the solvent being always potassium iodide. Solutions were

tried containing from about  $1\frac{1}{2}$  to 6 mols. of potassium iodide to one equivalent of iodine, with the object of ascertaining what effect, if any, the presence of potassium iodide would have on the reaction.

When an alkali is added gradually to a strong solution of iodine in potassium iodide, the brown colour disappears rapidly at first, but presently the liquid becomes pale yellow, and the further addition of alkali produces very little alteration. The pale yellow colour is, of course, due to free iodine. The reaction being a balanced one, it is plain that a large excess of alkali would be required in order to absorb *all* the iodine. Naturally, also, the amount of alkali required would be greater the more potassium iodide there was present in the solution, and this, indeed, was the only effect which differences in the amount of potassium iodide caused; in every other respect, the different solutions of iodine which were used behaved practically alike. I ascertained that when the pale yellow coloration is reached the amount of free iodine present is certainly not more than 1 to 1.5 per cent. of the total amount, and consequently the reaction, whatever it is, has proceeded with 98—99 per cent. of the original iodine. I decided, therefore, that it would be better to ignore altogether the small amount of free iodine, rather than to add the large excess of alkali which would be necessary to entirely remove it; accordingly only that amount of alkali required to produce—as far as could be judged by the eye—always the same pale yellow colour was employed. I invariably noticed that, after a few minutes, the colour became paler and paler, the amount of free iodine evidently gradually diminishing; this will be readily understood from the description of the results.

In all the experiments, the method was to rapidly pour into 10 c.c. or more of the decinormal iodine solution the requisite amount of potash\* to produce the pale yellow colour. Then, either immediately or after any desired interval, the liquid was stirred up with excess of solid sodium hydrogen carbonate, and a little soda-water was run in from a "syphon." The effect of this is always to liberate an amount of iodine depending entirely on the amount of hypiodite present, the iodine liberated being twice the amount which existed as hypiodite. The liberated iodine was estimated by means of a decinormal solution of arsenious acid.

In one set of six experiments, the requisite amount of potash was added, as rapidly as possible, to the iodine solutions containing different amounts of potassium iodide, and then, as quickly as it could be done, a large excess of sodium hydrogen carbonate was added, and

\* The amount of potash required had been ascertained by previous experiments; it varied from 1.75 to 3.5 equivalents of potash to one of iodine, according to the amount of potassium iodide in the solution. The potash was used in the form of a semi-normal solution.

the liberated iodine determined. It varied, in the six experiments, from a minimum of 88 per cent. to a maximum of 91 per cent. of the original amount of iodine used.

In another similar set of six experiments, but using twice as much alkali in each case, the liberated iodine varied from a minimum of 90 per cent. to a maximum of 94 per cent. of the original amount.

It is plain that, in these experiments, over 90 per cent. of the iodine acted on potash as represented in the first equation (p. 726).

In another set of six experiments, using again twice the necessary amount of alkali, the mixture was allowed to stand for half a minute before adding the sodium hydrogen carbonate; in this case, the liberated iodine was only 69 to 73 per cent. of the original amount. With less potash, but again allowing to stand for half a minute, the iodine liberated varied from 45 to 53 per cent. of the original amount. When the mixture of iodine and alkali was allowed to stand for two minutes before adding the sodium hydrogen carbonate, the iodine liberated was only from 17 to 20 per cent. of the original amount.

It is plain that, in these strong solutions, the rate of decomposition of the hypiodite is excessively rapid, and, as it is impossible to perform the experiment so rapidly as not to allow a slight interval between the first mixing of the iodine and alkali and the subsequent addition of the sodium hydrogen carbonate, it is reasonable to conclude that, in the cases mentioned above where 90—94 per cent. of the iodine was liberated, *some* decomposition of hypiodite had already taken place. I think we are justified in concluding, therefore, that in strong as well as in dilute solutions, iodine and potash react normally, producing, in the first instance, nothing but hypiodite and iodide, the only difference between a strong and a dilute solution of iodine, when an alkali is added, being in the stability of the product.

That the stability of a hypiodite is greater when the solution is dilute was further proved by diluting the various iodine solutions before adding the alkali, when it was invariably found that the rate of decomposition of the hypiodite diminished with the degree of dilution. If a centinormal solution of iodine is used, and the requisite amount of alkali added, as much as 44 per cent. of the possible amount of hypiodite remains at the end of 5 minutes.

The above experiments were performed when the temperature of the laboratory was about 15—18°. It is hardly necessary to state that in all cases a hypiodite decomposes almost instantaneously when boiled. The fact that the stability of a hypiodite is increased by a large excess of alkali has been previously pointed out by several observers.

The rapid decomposition of hypiodites in strong solutions explains the gradual diminution of the free iodine which I have already men-

tioned as taking place when not too much alkali is used in the first instance. The action of alkali on iodine being a balanced one, the amount of free iodine is influenced by the amount of hypoiodite present, and, as this amount rapidly diminishes, the hitherto free iodine acts in its turn on the alkali.

In my former paper, I referred at some length to a paper by Lunge and Schoch (*Ber.*, 1882, 15, 1883) on calcium hypoiodite, and expressed myself as doubtful whether they had actually obtained a hypoiodite by their method. These further experiments convince me that Lunge and Schoch's solutions did not contain more than a trace of hypoiodite. It is sufficient to mention that they prepared their solutions by rubbing together for some time solid iodine with a large excess of lime and very little water, allowed the product to stand for some hours, and then diluted with water. From what I have shown above as to the stability of hypoiodites in strong solutions, a method such as they described could not be successful.

It is plain also that the results of Péchard's attempts to find the relative amounts of hypoiodite and iodate in his solutions can be of very little value, seeing that his methods of determining them occupied a considerable time, and my experiments show that the amounts of hypoiodite and iodate would vary within a few seconds.

CENTRAL SCHOOL,  
MANCHESTER.

#### LXIV.—*Alkylation by means of Dry Silver Oxide and Alkyl Halides.*

By GEORGE DRUCE LANDER, D.Sc.

Dry silver oxide and alkyl iodides have been employed as an alkylating agent, by Purdie and Pitkeathly, in the preparation of alkyloxy- and dialkyloxy-succinic esters from malic and tartaric esters (*Trans.*, 1899, 75, 157), by Purdie and Irvine in the preparation of  $\alpha$ -alkyloxy-propionic esters from lactic esters (*Trans.*, 1899, 75, 485), and by McKenzie in the preparation of alkyloxyphenylacetic esters from mandelic esters (*Trans.*, 1899, 75, 754).

Apparently, the only prior applications of dry silver oxide as a synthetic agent are its use by Wurtz in the formation of ethyl ether from ethyl iodide (*Ann.Chim. Phys.*, 1856, [iii], 46, 222), and its applications in a similar sense by Erlenmeyer (*Annalen*, 1863, 126, 306), and Linnemann (*Annalen*, 1872, 161, 37).

The object of the present investigation was to ascertain to what

extent the use of dry silver oxide and alkyl halides is applicable to the production of alkyloxy-derivatives directly from hydroxy-compounds, and in general to the production of alkyl derivatives of compounds, of more or less well defined acid character, possessing hydrogen atoms replaceable by alkyl radicles.

The various methods of preparing alkyl derivatives of compounds falling within the assigned limits may be brought under two general headings:

1. The action on a hydroxy-compound of an alcohol, either alone, or in the presence of sulphuric or hydrochloric acid.

2. The action of alkyl halides on metallic derivatives, which, for the purposes of the synthesis, may or may not require to be isolated in the pure state.

To the first general method belong:

The formation of hydrolysable esters from acids by the action of alcohol, with or without the use of a mineral acid.

The formation of fatty ethers from alcohols by the action of alkyl hydrogen sulphates, or alkyl benzenesulphonates.

The formation of ethers of hydroxy-compounds  $R \cdot OH$ , in which  $R$  is not an aliphatic residue. As instances, may be quoted the preparation of benzoin ethers from benzoin, alcohol, and sulphuric acid (Fischer, *Ber.*, 1893, 26, 2412), and the production of glucosides (Fischer, *Ber.*, 1893, 26, 2401). The method does not appear to be applicable to the formation of alkyl derivatives of the simpler types of hydroxy-esters.

The mechanism of the reaction is doubtless the same in all cases, depending upon the formation of esters of the mineral acid containing the alkyl radicle introduced (conceivably also of the complex radicle itself). The general equation would be  $ROH + R'X = ROR' + HX$ .

To the second general method belong:

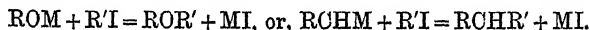
The formation of hydrolysable esters of acids by the action of alkyl halides on the sodium or, more usually, silver salts. To the same special case should also be referred the alkylation, through the intermediary of metallic derivatives, of such less distinctly acidic compounds as phenols, amides, imides, lactams, and lactims.

The formation of alkyl derivatives of compounds containing hydrogen atoms (labile or not) replaceable by alkyl groups by the action of alkyl iodides and sodium alkyloxides, represented most simply by ethyl acetoacetate and malonate, benzyl cyanide, and deoxybenzoin.

The formation of alkyl ethers from sodium alkyloxides and alkyl iodides. The cases of the formation of esters of alkyloxy-acids from halogen-substituted esters by the action of alkyloxides, for example, alkyloxypropionates (Schreiner, *Annalen*, 1879, 197, 12), and of alkyloxypropionates from sodiolactates by the action of alkyl iodides



(Wislicenus, *Annalen*, 1863, 125, 53), may be considered as also illustrating this special case. The general equation for the method would be :



It need scarcely be indicated that the above is not a hard and fast classification, as methods in particular instances may, and do, overlap. It is laid down as presenting a scheme, according to which the study of the action of silver oxide and halides has been directed.

### I. Action of Dry Silver Oxide and Ethyl Iodide on 1-Menthol.

The case of menthol is interesting as affording a means of testing the applicability of dry silver oxide and alkyl halides to the etherification of a secondary alcohol, and further, as affording a possible method for the preparation of optically active menthyl ethers.

Menthyl ethyl ether, presumably optically inactive, has been prepared by Brühl (*Ber.*, 1891, 24, 3376) from sodium menthyl oxide by the action of ethyl iodide. An experiment on a small scale showed that menthol is not etherified, even on prolonged boiling, by alcohol and concentrated sulphuric acid.

The menthol used in the following experiments melted at 42°, boiled at 211—212°, and in a 5.09 per cent. alcoholic solution had  $[\alpha]_D^{20} - 49.52^\circ$ . For a 5 per cent. alcoholic solution, Arth (*Ann. Chim. Phys.*, 1886, [vi], 7, 438) gives  $[\alpha]_D^{20} - 49.4^\circ$ .

A preliminary experiment with dry silver oxide and ethyl iodide showed that interaction had occurred. After three successive treatments with oxide and iodide, the product obtained was an oil of faint ethereal odour, giving  $\alpha - 82.33^\circ$  in a 100 mm. tube at 12°.

The preparation was therefore carried out on a larger scale. 111 grams of dry silver oxide ( $1\frac{1}{2}$  mols.) were added to the cold solution of 50 grams of menthol (1 mol.) in 150 grams of ethyl iodide (3 mols.). No action occurred in the cold. On warming to the boiling point on a steam-bath, reaction set in, as indicated by ebullition, which continued for one hour after removal from the source of heat. The mixture was subsequently boiled for 6 hours. Some water was formed in the course of the reaction. The solution was filtered, the silver residue washed repeatedly with ether, and, after removal of the ether, the liquid was distilled. The boiling point rose rapidly from 100° to 205°. The product boiling between 208° and 215°, amounting to 52 grams, was collected, and gave  $\alpha_D - 72.62^\circ$  in a 100 mm. tube at 11°.

The whole quantity (52 grams), together with 5 grams ( $\alpha_D - 82^\circ$ )

from the preliminary experiment, was again similarly treated with 74 grams of dry silver oxide and 100 grams of ethyl iodide. The reaction initiated on warming lasted 20 minutes; the boiling was continued for 8 hours. 52 grams of product, boiling between  $205^{\circ}$  and  $215^{\circ}$ , separated as above, were obtained, and gave  $\alpha_D - 82.22^{\circ}$  in a 100 mm. tube at  $11^{\circ}$ .

A third treatment with 60 grams of oxide and 80 grams of iodide, in which the initial action was very slight, and the boiling continued for 6 hours, gave 42 grams of substance boiling at  $208-213^{\circ}$ , which, in a 100 mm. tube at  $10.5^{\circ}$ , had  $\alpha_D - 83.01$ . The liquid product from the third treatment was heated on a water-bath before addition of the ethereal washings. The distillation of a small fraction below  $40^{\circ}$  indicated that in all probability ethyl ether had been formed in the reaction.

The product was fractionated in order to see whether notable increase in rotation could thereby be effected. Three fractions were collected, and the rotations were observed in a 100 mm. tube at  $10^{\circ}$ :

I. $205-207^{\circ}$ , about one-quarter .....	$\alpha_D - 79.93^{\circ}$ .
II. $207-209^{\circ}$ , main fraction.....	$\alpha_D - 84.35^{\circ}$ .
III. $209-212^{\circ}$ , small .....	$\alpha_D - 84.77^{\circ}$ .

Apparently, therefore, the rotation ( $-84.35^{\circ}$  to  $-84.77^{\circ}$ ) had reached a maximum. Fractions II and III were united and redistilled, but the lower fraction,  $205-207^{\circ}$ , was neglected, although nearly pure. Seventeen grams were collected between  $207.5^{\circ}$  and  $209.5^{\circ}$ , and taken as pure. The higher fraction was very small. Analysis of the pure product gave figures agreeing with those required for menthyl ethyl ether.

0.1041 gave 0.2978  $\text{CO}_2$  and 0.1220  $\text{H}_2\text{O}$ . C=78.02; H=13.02.

0.1334 „ 0.3821  $\text{CO}_2$  „ 0.1576  $\text{H}_2\text{O}$ . C=78.11; H=13.12.

$\text{C}_{12}\text{H}_{24}\text{O}$  requires C=78.26; H=13.04 per cent.

The specific rotation of the liquid at  $20^{\circ}$  was as follows:

$$\alpha_D = -83.94^{\circ}, l=1, d_{20^{\circ}/4^{\circ}}=0.8537, [\alpha]_D^{20} = -98.32^{\circ}.$$

## II. Attempts to prepare Ethers of Triphenylcarbinol.

The case of triphenylcarbinol may, in many respects, be regarded as crucial. On the one hand, it might be imagined that the presence of the three electronegative phenyl groups might confer fairly well defined acidic properties on the hydroxy-group; on the other, the great stability of the carbinol would no doubt render the substance less susceptible to the action of a reagent such as silver oxide and alkyl halides.

Pure triphenylcarbinol undergoes no change when boiled for 12 hours with dry silver oxide and either ethyl or isopropyl iodide. In the case of ethyl iodide, reaction of any kind is incomplete, although, without doubt, some ethyl ether is produced. Heated in a sealed tube with silver oxide and ethyl iodide at 160° for 4 hours, the carbinol underwent no change, but pure yellow silver iodide was obtained, and, under these conditions, the reaction between the oxide and iodide seems to be complete.

In the case of isopropyl iodide, the interaction at 100° is complete, as indicated by the formation of pure yellow silver iodide, after prolonged boiling with excess of iodide—18 grams of oxide gave 34 grams of iodide; calculated, 36.4 grams—and by the formation of a liquid boiling between 60° and 68° (isopropyl ether boils at 68.5—69°, according to Erlenmeyer, *loc. cit.*).

It is noteworthy that in no other reaction carried out under similar conditions is a pure yellow residue obtained, the residues being invariably dark coloured, brown or greenish-black.

Much delay was caused in the carrying out of the above experiments from the fact that the carbinol was contaminated with triphenylmethane. The recovery of the hydrocarbon indicates, however, that it is not acted upon by silver oxide and iodides, although the presence of three acidic groups united to the :CH residue renders it conceivable that the hydrogen of this radicle might be replaceable by alkyl groups.

### III. *Action of Dry Silver Oxide and Alkyl Iodides on Benzoin.*

Benzoin affords an instance of a hydroxy-compound, R.OH, in which the radicle R is not a hydrocarbon residue. It was therefore of interest to see whether, in this particular case, silver oxide and alkyl iodides would serve as an alkylating agent.

#### *Action of Silver Oxide and Ethyl Iodide on Benzoin.*

The ethyl ether of benzoin is described as one of the products of interaction of benzoin, ethyl alcohol, and sodium by Limpricht and Jena (*Annalen*, 1870, 155, 96), who ascribe to it the melting point 95°. It is also described as resulting from the action of ethyl alcohol and concentrated sulphuric acid on benzoin by Fischer (*loc. cit.*), who assigns to it the melting point 62°.

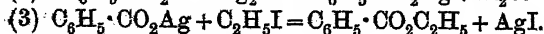
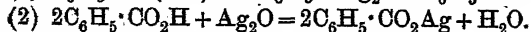
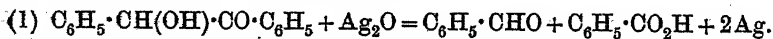
Preliminary experiments on the small scale showed that reaction occurred between benzoin, silver oxide, and ethyl iodide, as the benzoin, which is but sparingly soluble in the hot iodide, eventually dissolved in the mixture. In addition to some unchanged substance,

a solid of lower melting point, contaminated, however, with oily compounds smelling strongly of benzaldehyde, appeared to constitute the main product of the reaction. The following method was finally found most convenient for the isolation of the products.

Finely powdered benzoin (30 grams) was intimately mixed with dry silver oxide (40 grams, 7 grams in excess of the calculated amount) and ethyl iodide (54 grams, an excess of 10 grams) added. No change occurred even on standing one hour in the cold, but on raising to the boiling point, reaction set in, lasting of itself for about half an hour. The mixture was boiled in all for about four hours. During the operation, the benzoin passed into solution and did not crystallise out on cooling. Water was formed in the reaction, and the liquid acquired a distinct odour of benzaldehyde; the silver residue was dark coloured. The products of the reaction were extracted with ether, and after removal of ether on the water-bath, the residual oil was distilled in a vacuum. Two fractions were collected; the first was a liquid, boiling between 95° and 102° under 20—40 mm. pressure; the second an oil which speedily solidified on cooling and stirring, and boiled at 184—186° under 12 mm. pressure.

The liquid of low boiling point was redistilled under the ordinary pressure, whereby it was separated into two portions, the first boiling at 190—200°, the second at 200—207°. The fraction of boiling point 190—200° smelt strongly of benzaldehyde and had an acid reaction. A few drops exposed to the air rapidly went semi-solid, yielding an acid dissolved by sodium carbonate solution, from which it was reprecipitated by dilute sulphuric acid. Further evidence of its identity with benzaldehyde was obtained by the preparation of the compound with sodium hydrogen sulphite and of the phenylhydrazone.

The fraction of boiling point 200—207° was shaken out repeatedly with concentrated sodium hydrogen sulphite, and from the ethereal solution of the residual oil sodium carbonate solution extracted practically no benzoic acid. On hydrolysing this oil (5.5 grams) with 10 per cent. potassium hydroxide solution, with addition of alcohol, 3.5 grams of benzoic acid were obtained melting at 120°. It is thus evident that one phase of the reaction of dry silver oxide and ethyl iodide on benzoin consists in the partial oxidation of the benzoin, resulting in the formation of benzaldehyde and ethyl benzoate, as may be indicated by the following equations:



The residue left in the flask after distillation of the original product in a vacuum was small. On twice recrystallising it from alcohol

a crop of needles melting at 120° to 126° (impure benzoin) was obtained.

The solid substance boiling at 184—186° in a vacuum weighed 12 grams. It could be crystallised either from alcohol or light petroleum, and was purified for analysis by recrystallisation from the latter, in which it is easily soluble on boiling. The compound separates, on standing, in warty aggregates of fine needles, and, after recrystallisation, melts at 58—58·5°. Analysis gave figures agreeing with those required by the formula  $C_6H_5 \cdot CH(OC_2H_5) \cdot CO \cdot C_6H_5$ .

0·2285 gave 0·6695  $CO_2$  and 0·1465  $H_2O$ . C = 79·90; H = 7·12.

0·1683 „ 0·4940  $CO_2$  „ 0·1030  $H_2O$ . C = 80·04; H = 6·80.

$C_{16}H_{16}O_2$  requires C = 80·00; H = 6·66 per cent.

*Action of Isopropyl Iodide and Dry Silver Oxide on Benzoin.*

Twenty-two grams of benzoin, 28 grams (5 grams in excess) of dry silver oxide, and 41 grams (7 grams in excess) of isopropyl iodide were used. As the whole of the benzoin did not dissolve in the iodide when heated, 20 grams of benzene were added to nearly complete its solution. On adding half of the oxide to the warm liquid, vigorous action occurred, lasting, however, only a few minutes. After cooling, the remainder of the oxide was added, and a reaction lasting about a quarter of an hour set in. The mixture was subsequently boiled for 2 hours, and, on cooling, needles resembling benzoin in crystalline form were deposited. A further quantity of 10 grams of oxide and 15 grams of iodide was therefore added, which induced further action, lasting 20 minutes. The mixture was finally boiled for 3 hours, the warm liquid filtered, and the residue washed with ether. On cooling the benzene solution, a separation of needles occurred, which, after recrystallisation from alcohol, melted at 128—132°, and consisted of unchanged benzoin. The viscid liquid left after distilling off the solvent, was separated as far as possible from deposited benzoin, and distilled in a vacuum. As in the case of the reaction of the oxide and ethyl iodide, a fraction boiling below 100° under about 20 mm. pressure was collected, which proved to be a mixture of benzaldehyde and isopropyl benzoate. From the fraction above 100°, 7 grams of a liquid easily solidifying on cooling and stirring, and fusing below 100°, were obtained, boiling from 175—180° under 10 mm. pressure. This was purified by recrystallisation from light petroleum, one volume of the fused substance being easily soluble in about three volumes of the hot solvent and was obtained in aggregates of minute needles melting at 72—75°. The melting point was not altered by recrystallisation. The substance reduced Fehling's solution very slightly upon boiling, owing, possibly, to the presence of unchanged benzoin in quantities too

small for detection. Analysis gave figures agreeing with those required for the isopropyl ether of benzoin.

0.1408 gave 0.4132  $\text{CO}_2$  and 0.0912  $\text{H}_2\text{O}$ .  $\text{C} = 80.03$ ;  $\text{H} = 7.19$ .

0.1380 „ 0.4056  $\text{CO}_2$  „ 0.0883  $\text{H}_2\text{O}$ .  $\text{C} = 80.15$ ;  $\text{H} = 7.11$ .

$\text{C}_{17}\text{H}_{18}\text{O}_2$  requires  $\text{C} = 80.31$ ;  $\text{H} = 7.08$  per cent.

The somewhat greater proportion of benzoin, which escapes reaction in the case of isopropyl iodide, as compared with that of ethyl iodide, may be due to the dilution brought about by the use of benzene, but in greater likelihood is attributable to the superior facility with which isopropyl iodide interacts with silver oxide.

#### IV. *Action of Dry Silver Oxide and Alkyl Iodides on Amides.*

The alkylation of amides and allied substances presents considerable analogy to the esterification of acids by the action of alkyl halides on metallic salts, as in many instances the silver or other salts can be isolated in a pure state, and submitted to the action of alkyl halides (compare Tafel and Enoch, *Ber.*, 1890, 23, 103). In contradistinction to the comparatively simple case of the metallic salts of carboxylic acids, the metallic salts of amides, &c., may correspond to the labile form of the free compound. In particular does this seem to be the case with the silver salts (Tafel and Enoch, *loc. cit.*).

The object of studying the action of silver oxide and alkyl iodides on amides was to ascertain whether the intermediate step of preparation and isolation of the silver salt could not be obviated, and iminoethers be prepared directly from amides by the use of this reagent.

#### *Action of Silver Oxide and Ethyl Iodide on Benzamide.*

Ethyl benzimino-ether has been prepared from benzonitrile by the action of ethyl alcohol and dry hydrochloric acid (Pinner, *Ber.*, 1883, 16, 1654), and from silver benzamide by the action of ethyl iodide (Tafel and Enoch, *loc. cit.*).

Assuming the reaction to proceed through the formation of silver benzamide, the production of water in the reaction  $2\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{NH}_2 + \text{Ag}_2\text{O} = 2\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{NHAg} + \text{H}_2\text{O}$  would tend to regenerate amide from any imino-ether which might have been formed. It seemed probable, however, that by using a considerable excess of oxide and iodide, the water thus formed might be removed from the sphere of action thus,  $\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2\text{C}_2\text{H}_5\text{I} = 2\text{AgI} + 2\text{C}_2\text{H}_5 \cdot \text{OH}$ .

Twelve grams of benzamide, 46 grams of dry silver oxide (calculated 11.6 grams), and 62 grams of ethyl iodide were used. The benzamide was added to the iodide and the liquid warmed, but as solution was incomplete, 20 grams more iodide were added, and, on warming, nearly

the whole of the amide then passed into solution. After addition of the powdered oxide, the liquid was raised to the boiling point when reaction set in, and continued without application of heat for half an hour. After this had subsided, the mixture was boiled for one hour. Water was formed in the reaction, but on continued boiling it disappeared. The silver residue was greenish-yellow. The solution was filtered, and the residue washed with dry ether, the washings being added to the original solution. The liquid had a characteristic odour, and showed no tendency to crystallise on standing. Addition of a slight excess of an ethereal solution of hydrogen chloride caused the precipitation of a crop of fine needles, weighing 7 grams, which melted at 118—120° with evolution of gas, fusing somewhat higher after resolidification. The hydrochloride was further purified by solution in as small a quantity of alcohol as possible, and reprecipitation by dry ether. The chlorine in the air-dried substance was estimated by titration with decinormal silver nitrate solution.

0.2917 required 15.90 c.c.  $\text{AgNO}_3$ .  $\text{Cl} = 19.35$ .

0.3481 „ 18.85 c.c.  $\text{AgNO}_3$ .  $\text{Cl} = 19.22$ .

$\text{C}_6\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5) \cdot \text{NH}_2 \cdot \text{HCl}$  requires  $\text{Cl} = 19.13$  per cent.

The purified hydrochloride fused at 119—120° with evolution of gas, and after resolidification at 125° (compare Pinner, *loc. cit.*).

#### *Action of Silver Oxide and Ethyl Iodide on Acetanilide.*

The examination of the action of the oxide and iodide on acetanilide was undertaken in the hope that it would run a course parallel to that of benzamide, and yield N-phenylacetiminoethyl ether or ethyl isoacetanilide,  $\text{C}_6\text{H}_5 \cdot \text{N} \cdot \text{C}(\text{O} \cdot \text{C}_2\text{H}_5) \cdot \text{CH}_3$ . Silver formanilide corresponds to the iso-type, yielding iso-ethers by the action of alkyl iodides (Comstock and Kleeberg, *Amer. Chem. J.*, 1879, 12, 498). In contradistinction to sodium acetanilide,  $\text{C}_6\text{H}_5 \cdot \text{NNa} \cdot \text{CO} \cdot \text{CH}_3$ , silver acetanilide, upon the formation of which the reaction depends, would almost certainly be  $\text{C}_6\text{H}_5 \cdot \text{N} \cdot \text{C}(\text{OAg}) \cdot \text{CH}_3$ .

Thirteen and a half grams (1 mol.) of acetanilide were dissolved in 47 grams (3 mols.) of hot ethyl iodide, and 35 grams ( $1\frac{1}{2}$  mols.) of dry silver oxide were added in small portions to the hot solution. The addition of each portion induced a moderate reaction, which, after all the oxide had been added, lasted half an hour. The mixture was subsequently boiled for one hour, and the product extracted repeatedly by dry ether. After removal of ether on the water-bath, the liquid was left for 24 hours, during which time some unchanged acetanilide was deposited. The remaining liquid was fractionated in a vacuum. The main fraction boiled at 99—100° under 10 mm. pressure, weighed

9 grams, and was a colourless, mobile liquid smelling of geranium; it displayed no tendency to solidify, either upon cooling or after prolonged standing. In addition to this liquid product, a further small quantity of acetanilide was obtained.

The liquid was analysed.

0.2084 gave 0.5600  $\text{CO}_2$  and 0.1510  $\text{H}_2\text{O}$ .  $\text{C}=73.28$ ;  $\text{H}=8.05$ .

0.1556 „ 0.4192  $\text{CO}_2$  „ 0.1134  $\text{H}_2\text{O}$ .  $\text{C}=73.47$ ;  $\text{H}=8.09$ .

0.2370 „ 18.0 c.c. moist nitrogen at  $5.5^\circ$  and 733 mm.  $\text{N}=8.92$ .  
 $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{C}(\text{O}\cdot\text{C}_2\text{H}_5)\cdot\text{CH}_3$  requires  $\text{C}=73.62$ ;  $\text{H}=7.97$ ;  $\text{N}=8.59$  per cent.

The boiling point of ethyl isoacetanilide under the ordinary pressure is  $207-208^\circ$ . The compound is extremely easily hydrolysed by dilute hydrochloric acid, in which it dissolves rapidly in the cold, and on addition of an excess of platinum chloride to the solution, aniline platinichloride separates in aggregates of blade-like crystals ( $\text{Pt}=32.60$ ; calculated  $32.69$  per cent.). This, when shaken with sodium hydroxide solution, gave an oil which coloured calcium hypochlorite solution purple.

On warming a solution of ethyl isoacetanilide for a few moments with concentrated hydrochloric acid, the smell of ethyl acetate was perceptible, and, on cooling, crystals of aniline hydrochloride were deposited.

Like methyl isoformanilide (Comstock and Kleeberg, *loc. cit.*), it yields an amidine by interaction with aniline. Ethyl isoacetanilide (3 grams) was warmed for 5 hours on the water-bath with aniline (2 grams), and the reaction completed by boiling the liquid for a few moments; on cooling, the substance solidified, and was identified as diphenylmethylamidine, melting at  $131-132^\circ$  (Biedermann, *Ber.*, 1874, 7, 540). Four grams of amidine were produced.

0.1910 gave 22.0 c.c. moist nitrogen at  $4^\circ$  and 723 mm.  $\text{N}=13.43$ .  
 $\text{C}_{14}\text{H}_{14}\text{N}_2$  requires  $\text{N}=13.33$  per cent.

#### V. Action of Dry Silver Oxide and Ethyl Iodide on Ethyl Acetoacetate.

The alkylation of ethyl acetoacetate by the action of silver oxide and alkyl iodides, in addition to serving as an instance of the application of the method to this particular class of compound, is of special interest as affording a possible means for the production of the isomeric ethers in place of the alkyl compounds formed by the action of sodium ethoxide and alkyl iodides. From the fact that silver oxide and iodides effect the direct etherification of the alcoholic hydroxy-group of certain compounds, it seemed quite likely that in the interaction (if any) with ethyl acetoacetate the latter would react



in the enolic form as ethyl  $\beta$ -hydroxycrotonate, and that the product would be ethyl  $\beta$ -ethoxycrotonate. The methoxy-compound has been obtained by the alkylation of ethyl acetoacetate by diazomethane, a reagent which lends itself to the formation of ethers of hydroxy-compounds of acid or feebly acid character (von Pechmann, *Ber.*, 1895, 28, 1624); the ethoxy-derivative by the action of sodium ethoxide on ethyl  $\beta$ -isochlorocrotonate (Friedrich, *Annalen*, 1883, 219, 333), and from ethyl acetoacetate by interaction with ethyl orthoformate (Claisen, *Ber.*, 1896, 29, 1006).

After preliminary experiments with from 20 to 50 grams of ethyl acetoacetate had shown that the product of the interaction with silver oxide and ethyl iodide was mainly ethyl ethylacetoacetate, mixed, however, with a very small proportion of ethyl  $\beta$ -ethoxycrotonate, the following preparation on a large scale was carried out with the object of isolating the latter in a state of purity. Dry silver oxide (174 grams) was added in small portions to a mixture of ethyl acetoacetate (90 grams) and ethyl iodide (237 grams). On warming, after the addition of the first portion of oxide, a vigorous action set in, which was moderated by cooling from time to time with water. After all the oxide had been added and the spontaneous reaction had ceased, the mixture was boiled for 45 minutes. Some water was formed in the reaction. The liquid was filtered, the residue washed four times with ether, and the ethereal solution fractionated after drying over anhydrous sodium sulphate. After removal of ether and excess of iodide, the boiling point rose rapidly to  $190^{\circ}$ , and 75 grams boiling at  $190$ — $198^{\circ}$ , together with 9 grams boiling at  $198$ — $205^{\circ}$ , were collected. The residue in the distillation flask was small. As both fractions gave a violet colour with alcoholic ferric chloride, they were united, and the ethyl ethylacetoacetate removed by hydrolysis with 60 grams of potassium hydroxide dissolved in 600 c.c. of water. On shaking and warming, nearly all the ester passed into solution, and on further heating a clear, oily layer (ketone) separated. In all, the liquid was heated for less than half an hour. The ketone and unchanged ester were extracted by shaking out twice with ether, and the ethereal solution, after being dried over calcium chloride, was distilled. After removal of the ether on the water-bath, the ketone was distilled off below  $110^{\circ}$ , a small fraction was collected between  $110^{\circ}$  and  $186^{\circ}$ , and the remainder between  $186^{\circ}$  and  $190^{\circ}$ . The last fraction gave no coloration with ferric chloride, and on cooling solidified almost completely in tabular crystals, which only partially fused on standing at the temperature of the laboratory. The nearly solid substance was drained as far as possible on the filter pump, and washed with a small quantity of ether. The crystals thus obtained were rather moist, but after pressing on filter paper melted

at 29—30° and were identified as ethyl  $\beta$ -ethoxycrotonate (compare Friedrich, *loc. cit.*). On analysis:

0.1554 gave 0.3461  $\text{CO}_2$  and 0.1256  $\text{H}_2\text{O}$ .  $\text{C} = 60.74$ ;  $\text{H} = 8.98$ .

$\text{C}_8\text{H}_{14}\text{O}_3$  requires  $\text{C} = 60.76$ ;  $\text{H} = 8.86$  per cent.

On prolonged standing, the crotonate separated in long, rectangular plates from the impure liquors, removed in the preparation of a pure sample. That the substance was ethyl  $\beta$ -ethoxycrotonate, and not ethyl ethylacetoacetate, was further shown by the facts that it gave no colour with ferric chloride, and that, on hydrolysis with potassium hydroxide, an acid melting and decomposing at 137.5° was obtained.

The alkaline solution, obtained in the removal of the ethyl ethylacetoacetate, upon cautious acidification in the cold with dilute sulphuric acid, yielded a small quantity of  $\beta$ -ethoxycrotonic acid, which separated on spontaneous evaporation of an ethereal solution in well defined, prismatic crystals melting and decomposing at 137.5°. The total quantity of  $\beta$ -ethoxycrotonate formed in the reaction was, as far as could be ascertained, not more than 5 grams, or about 5 per cent. of the whole.

Sodium  $\beta$ -ethoxycrotonate is decomposed on warming in aqueous solution. It is conceivable that any crotonate produced in the alkylation of ethyl acetoacetate by sodium ethoxide might be decomposed in the process of separation, owing to the presence of adventitious traces of hydroxide. The alkylation of ethyl acetoacetate was therefore effected by the aid of potassium ethoxide and ethyl iodide, and the ester examined by the method of hydrolysis described in the case of the silver oxide product. A small quantity of a liquid, which boiled at 210—214°, gave no colour with ferric chloride, and dissolved in potassium hydroxide solution with separation of an oil, was obtained on distilling the methyl propyl ketone and non-hydrolysed oil. This was in all probability ethyl diethylacetoacetate (b. p. 218°). From the alkaline liquor, dilute sulphuric acid precipitated an oily acid, which on long standing partially solidified, the solid melting at 109° without decomposition. It was probably dehydracetic acid (n. p. 108.5—109°), and the quantity was extremely small. No trace of  $\beta$ -ethoxycrotonic acid could be detected.

Modification of the method of carrying out the alkylation of ethyl acetoacetate by means of silver oxide may result in the reaction pursuing a different course, as in the following instance, in which the ethyl iodide was added to the mixture of ester and oxide. The addition of a small quantity of iodide caused a considerable rise in temperature, white fumes appearing in the flask. As it was desired to keep down the temperature, benzene was added, and then the remainder of the iodide was introduced in small quantities. The reaction was

completed by heating for a short time on the steam-bath. More water was formed than in the case of the addition of the oxide to the ester and iodide (p. 739). After removal of benzene and iodide, the ester, which gave a reddish-violet tint with alcoholic ferric chloride, was distilled off. A considerable residue remained in the flask. After standing all night, it partially solidified to needles. In a vacuum, about half of this residue distilled over at approximately  $210^{\circ}$  under 20 mm. pressure. This distillate was crystallised from light petroleum, from which it separated in fine needles melting at  $102\text{--}105^{\circ}$ . Only 0.7 gram was obtained from 65 grams of ethyl acetoacetate, and after recrystallisation from ether, this gave 0.5 gram, melting at  $103\text{--}106^{\circ}$ . The substance gave a deep blue tint with alcoholic ferric chloride.

Analysis gave figures agreeing best with those required for ethyl diacetylfumarate.

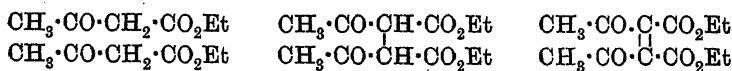
0.1646 gave 0.3420  $\text{CO}_2$  and 0.0912  $\text{H}_2\text{O}$ . C = 56.66 ; H = 6.15.

0.1578 „ 0.3263  $\text{CO}_2$  „ 0.0840  $\text{H}_2\text{O}$ . C = 56.39 ; H = 5.91.

$\text{C}_{12}\text{H}_{16}\text{O}_6$  requires C = 56.26 ; H = 6.25 per cent.

No other product could be isolated in a state of purity from the oily residue of high boiling point.

Ethyl diacetylfumarate (m. p.  $95.5\text{--}96^{\circ}$ ) has been prepared by the action of iodine on ethyl sodiodiacetylsuccinate (Just, *Ber.*, 1885, 18, 2636), and by the action of finely divided silver on ethyl iodoacetoacetate (Schönbrodt, *Annalen*, 1889, 253, 196). Its formation in the action of silver oxide on ethyl acetoacetate is readily explicable, if it is regarded as produced by oxidation, either directly or through the intermediary of ethyl diacetosuccinate :



Attempts to obtain the acid by hydrolysis with alcoholic potassium hydroxide, resulted only in the production of resinous matter (compare Paal and Härtel, *Ber.*, 1897, 30, 1994).

#### *Action of Silver Oxide and Ethyl Iodide on Ethyl Ethylacetoacetate.*

Alkylation of ethyl ethylacetoacetate by silver oxide and ethyl iodide seems to occur, but only to a very slight extent. Forty-eight grams of ethyl ethylacetoacetate (b. p.  $193\text{--}195^{\circ}$ ) were boiled with 70 grams of silver oxide and 94 grams of ethyl iodide for 3 hours. The silver residue weighed 112 grams (calculated 142). The ester was separated into three fractions, the first, boiling at  $195\text{--}198^{\circ}$ , constituted the main fraction ; the others were small, and boiled at  $198\text{--}203^{\circ}$  and  $203\text{--}214^{\circ}$ . All three coloured alcoholic ferric chloride violet. By

partial hydrolysis, a small quantity (about 6 grams) of ester boiling at 204—214° was obtained. It gave no colour with ferric chloride, and on boiling with aqueous potassium hydroxide, gave a non-hydrolysable oil (ketone). No solid acid could be detected among the products of complete hydrolysis. Apparently, the homologue of ethyl  $\beta$ -ethoxycrotonate is not one of the products, or, at any rate, if formed, is produced only in very minute quantities.

#### VI. *Action of Dry Silver Oxide and Ethyl Iodoacetate on Ethyl Acetoacetate.*

The following experiment was undertaken in order to ascertain whether, in the synthesis of ethyl acetosuccinate from ethyl acetoacetate by the aid of sodium ethoxide and halogen substituted ethyl acetates, silver oxide could be employed in place of sodium ethoxide.

Various experiments had indicated that the use of chloro- or bromo-compounds gives less satisfactory results than that of iodo-derivatives. Ethyl iodoacetate, prepared by the action of potassium iodide on the chloroacetate, was therefore employed in preference to chloroacetate; its boiling point was 170—180°, and it probably contained some chloroacetate. Dry silver oxide (23 grams) was added in two portions to a mixture of 13 grams of ethyl acetoacetate and 21 grams of ethyl iodoacetate. After the reaction had been started on the water-bath, the liquid became very warm, and the flask was therefore cooled to moderate the action. A black deposit, purple by transmitted light, formed on the flask, indicating that metallic silver had in all probability been formed. After the reaction had moderated, benzene was added, and the liquid boiled for some time on the water-bath. Water was formed in the reaction. The solution was filtered, and the residue, which was very dark coloured, was washed with ether. After removal of the solvent, the oily residue was distilled in a vacuum. The main fraction, weighing 8 grams, boiled at 142—144° under 16 mm. pressure, and was an oil of faint, sweetish odour; one drop gave a distinct reddish-violet tint to an alcoholic solution of ferric chloride. As ethyl acetosuccinate gives no coloration with this agent (Conrad, *Annalen*, 1877, 188, 220), it was thought possible that the coloration might be due to the presence of traces of ethyl acetoacetate, but after redistillation in a vacuum, the same tint was given. Analysis gave figures agreeing with those required for ethyl acetosuccinate.

0.1833 gave 0.3715  $\text{CO}_2$  and 0.1231  $\text{H}_2\text{O}$ .  $\text{C} = 55.27$ ;  $\text{H} = 7.46$ .

$\text{C}_{10}\text{H}_{16}\text{O}_5$  requires  $\text{C} = 55.55$ ;  $\text{H} = 7.40$  per cent.

On hydrolysis with strong alcoholic potassium hydroxide, the substance gave succinic acid, melting at 179°, which was converted into barium salt. This was dried at 130° and analysed.

0.1265 gave 0.1159  $\text{BaSO}_4$ . Ba = 53.85.

$\text{C}_4\text{H}_4\text{O}_4\text{Ba}$  requires Ba = 54.22 per cent.

A second preparation was undertaken, in order to ascertain whether better yields of the acetosuccinate could be obtained. The silver oxide (46 grams) was added in the cold, and in small portions, to a mixture of 26 grams of ethyl acetoacetate and 43 grams of ethyl iodoacetate. The temperature of the liquid rose considerably on addition of each portion of oxide, and the action was allowed to subside before the next portion was added; 18 grams of acetosuccinate were obtained. The residue in the distillation flask was large. It did not solidify on prolonged standing, and, on attempting to distil it in a vacuum, partial decomposition occurred. A small quantity of a viscid oil distilled over below  $210^\circ$  under 17 mm. pressure, and a thick, tarry residue remained in the flask.

It seemed difficult to account for the fact that the acetosuccinate, prepared as above, gives a distinct coloration with alcoholic ferric chloride. This cannot be due to the presence of traces of oxidation products such as ethyl diacetofumarate, as redistillation does not deprive the compound of this property, and as the coloration is still given after the compound has been dissolved in sodium hydroxide and reprecipitated by acid. The explanation is to be found in the fact that, when prepared by the action of ethyl chloroacetate on ethyl sodioacetoacetate, the acetosuccinate is distinctly acid after distillation in a vacuum, whereas the product as obtained by the silver oxide method is almost exactly neutral. A sample of ethyl acetosuccinate, prepared by the aid of sodium ethoxide and giving no colour with ferric chloride, was shaken with sodium carbonate solution, in which it is insoluble. The neutral ether thus obtained coloured alcoholic ferric chloride in precisely the same way as the silver oxide product. The coloration given by neutral ethyl acetosuccinate is immediately discharged by the addition of a trace of hydrochloric acid; it is reproduced by the addition of a minute quantity of sodium carbonate, but again discharged by an excess of alkali. The coloration given to alcoholic ferric chloride by other substances, such as ethyl acetoacetate and salicylic acid, is similarly destroyed by the presence of free acid or alkali; thus, the red coloration of ethyl acetoacetate is destroyed by a trace of piperidine, reproduced by neutralisation with hydrochloric acid, and destroyed by an excess of hydrochloric acid.

#### VII. *Action of Silver Oxide and Ethyl Iodide on Ethyl Malonate.*

Ethyl malonate presents an instance of a ketonic compound which might exist in the labile hydroxy-form. That the substance does not

react in the hydroxy-form is shown by the fact that diazomethane is without action on it (von Pechmann, *loc. cit.*, 1628). Claisen (*Ber.*, 1892, 25, 1764) has further pointed out that the replacement of a hydrogen atom of the methyl group of ethyl acetate by the feebly negative carbethoxy-group is likely to lead to the formation of a compound behaving solely in accordance with the ketonic structure. In event of the malonate reacting with the oxide and iodide in the labile form  $\text{EtO} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \\ \text{HO} \end{array} \text{CH} \cdot \text{CO}_2\text{Et}$ , the product would be a  $\beta$ -diethoxyacrylate,

which on hydrolysis with potassium hydroxide would in all probability yield  $\beta$ -diethoxyacrylic acid, but under these conditions might also give, by elimination of the ethyl groups attached to oxygen, dihydroxyacrylic, that is, malonic, acid.

Preliminary experiments showed that interaction, if any, was very incomplete, but sufficient indication of the formation of ethyl ethylmalonate was afforded to justify the attempt to isolate it from the product. Sixty-nine grams of dry silver oxide ( $1\frac{1}{2}$  mols.) were added to a mixture of 32 grams (1 mol.) of ethyl malonate and 93 grams (3 mols.) of ethyl iodide. Reaction, as indicated by moderate ebullition, was started by warming on the steam-bath, and lasted of itself for half an hour, the mixture being subsequently boiled for 5 hours. No water could be detected in the product, and the silver residue, which was dark brown, weighed 126 grams (calculated 141 grams). By distillation, 28 grams of ester boiling at  $192-203^\circ$  were obtained. The residue in the distillation flask was very small, indicating that oxidation had not occurred to any considerable extent. The ester was subjected to partial hydrolysis by boiling with a solution of 15 grams of potassium hydroxide in 60 c.c. of water for 1 hour, and allowing to stand, with frequent shaking, for 24 hours. The non-hydrolysed oil was extracted with ether, and the ethereal solution, after drying with calcium chloride, on distillation gave 2 grams boiling at  $195-203^\circ$  (rejected), and 8 grams boiling at  $203-206^\circ$ . The latter fraction was hydrolysed by boiling with 7 grams of potassium hydroxide dissolved in 20 c.c. of water, sufficient alcohol being added to secure the solution of the oil. The resulting alkaline solution was neutralised by the addition of hydrochloric acid and ammonium hydroxide, and the boiling liquid precipitated by a hot concentrated solution of 8 grams of calcium chloride. The amorphous calcium salt thus obtained was washed with boiling water until free from chloride. A portion dried at  $120^\circ$  was analysed.

0.3738 gave 0.2986  $\text{CaSO}_4$ . Found  $\text{Ca} = 23.49$ .

$\text{C}_2\text{H}_5 \cdot \text{CH}(\text{CO}_2)_2\text{Ca}$  requires  $\text{Ca} = 23.53$  per cent.

That the salt was calcium ethylmalonate was further shown by de-

composing a portion with concentrated hydrochloric acid, and extracting with ether. On evaporation of the ether, a crystalline acid was left, which after drying on a porous tile melted at  $111.5^{\circ}$ , and commenced to decompose at  $160^{\circ}$ .

VIII. *Action of Dry Silver Oxide and Methyl Iodide on Salicylic Acid.*

The comparatively strong acidic character of phenolic hydroxyl rendered it practically certain that alkylation of phenols can be effected by means of silver oxide and iodides. Salicylic acid was selected for examination, as containing carboxyl in addition to the phenolic hydroxy-group, and therefore further serving to illustrate the esterification of acids by the use of the reagent. Moreover, the products obtained by the silver oxide method being usually very pure and free from resinous matter, the application of the method to phenolic substances was likely to lead to the formation of compounds free from the resinous matter generally produced by the application of potassium hydroxide and iodides. The interaction of 50 grams of silver oxide and a solution of 20 grams of salicylic acid in 62 grams of methyl iodide and 40 c.c. of benzene was very vigorous, but incomplete. The resulting ester, 17.5 grams, was neutral, and consisted of a mixture of methyl esters of salicylic and methoxybenzoic acids, as shown by the irregularity of the boiling point ( $228-240^{\circ}$ ), and by the production on hydrolysis of an acid which melted at  $100-130^{\circ}$ , and gave a violet colour with neutral aqueous ferric chloride. 12.5 grams of the mixed esters were therefore again treated with 20 grams of oxide and 25 grams of methyl iodide. No water was formed in the second treatment. By extraction of the oily products with ether and distillation, 12 grams of methyl methoxybenzoate boiling at  $245^{\circ}$  were obtained, the boiling point being given as  $228^{\circ}$  by Fölsing (*Ber.*, 1884, 17, 486). Five grams of the ester were hydrolysed by warming with a solution of 5 grams of potassium hydroxide in 20 c.c. of water, until the disappearance of oil. By acidification, 4.5 grams of methoxybenzoic acid, giving no colour with ferric chloride, were obtained. The acid was further purified by solution in a small quantity of warm alcohol and addition of about 3 volumes of water; on cooling, it was deposited in lustrous prisms melting at  $99^{\circ}$ . The following results were obtained on analysis:

0.1504 gave 0.3470  $\text{CO}_2$  and 0.0721  $\text{H}_2\text{O}$ . C = 62.92; H = 5.32.

$\text{C}_8\text{H}_8\text{O}_3$  requires C = 63.15; H = 5.26 per cent.

The production of the pure ester in one operation could apparently have been effected by employment of a larger excess of oxide, in

which case, too, the yield would probably have been better. The use of silver oxide and methyl iodide leads to the formation of a very clean product.

#### IX. *Action of Silver Oxide and Ethyl Iodide on Benzaldehyde.*

Since the action of silver oxide frequently results in oxidation, the following experiment was carried out in order to see whether it would be possible to effect the oxidation of an aldehyde and esterification of the acid in one operation. Fifteen grams of benzaldehyde, 35 grams of silver oxide, and 48 grams of ethyl iodide were used, and the reaction was very vigorous; the silver residue weighed 50 grams. From the proportions taken, it was to be expected that one-half of the aldehyde would be oxidised and esterified. The product was a mixture of benzaldehyde and ethyl benzoate. After the removal of the greater part of the aldehyde by fractionation, the ester was freed from traces of aldehyde by repeated extraction with sodium hydrogen sulphite solution. Ethyl benzoate boiling at  $206^{\circ}$  and yielding on hydrolysis benzoic acid melting at  $121^{\circ}$  was thus obtained.

#### *Discussion of Results.*

With respect to the general aspects of the behaviour of silver oxide and alkyl halides as an alkylating agent, it may be remarked that the course of the reaction is usually smooth and rapid. In many instances, complete alkylation is not effected by one treatment, and in others, for example, that of benzoin, the reaction may be slower owing to the insolubility of the substance to be alkylated. The limit of applicability may be regarded as reached in the cases of compounds insoluble in the halide or some neutral solvent. The difficulty of removing inorganic by-products is reduced to a minimum. In the case of the esterification of acids by the aid of mineral acids, or of acids whose silver salts are unstable, the direct application of silver oxide and alkyl iodides would doubtless secure considerable saving, both in time and material. The possibly prejudicial effect of the water usually formed in the reaction is, to a great extent, mitigated by the practical insolubility of water in the halide, and may, in certain cases, be reduced to a minimum by the employment of a sufficient excess of silver oxide and halide.

It will be seen that the reaction is applicable to the alkylation of typical compounds of all the classes enumerated in the introduction. It is apparently the only reaction whereby direct alkylation of the esters of hydroxy-acids may be brought about.

As regards the suitability of particular halides, iodo-compounds are



found to yield the best results. This is due no doubt in great measure to the inferior stability and consequently readier resolution of iodo- as compared with bromo- and chloro-derivatives. It is possible, however, that a connection may be traced between the fact that the molecular volume of silver iodide is greater than the sum of the atomic volumes of silver and iodine (in other words, there is an expansion in the formation of silver iodide), and the generally observed fact that the elimination of silver iodide in processes of organic synthesis is marked by especial ease. So far as our knowledge of the conditions modifying chemical change goes, it can only be said that this is a coincidence; the two facts may, however, be causally related. In this connection, it is of interest to note that similar volume relations hold for mercuric iodide, and mercuric oxide has been shown to be capable of use instead of silver oxide in the alkylation of ethyl malate (Purdie and Pitkeathly, *loc. cit.*, 157). The tardier action of chloro- and bromo-compounds is, moreover, detrimental, as greater chances are thereby afforded for the occurrence of reactions involving oxidation. Of the alkyl iodides, methyl and ethyl are most suitable, and of these the former lends itself more readily to the reaction than the latter. With isopropyl iodide, the reaction is usually not so complete, for example, in the case of benzoin. This may quite readily be accounted for by the fact that the interaction with silver oxide, with formation of alkyl ethers, is notably less vigorous in the cases of methyl and ethyl than in that of isopropyl iodide.

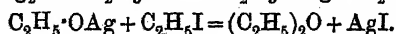
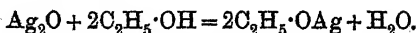
The phenomena of oxidation depend greatly, as was shown in the alkylation of ethyl acetoacetate, upon the conditions under which the experiment is carried out. That oxidation should occur is quite conceivable; in the absence of alkyl iodides, oxidation is extremely vigorous, usually resulting in the production of resinous matter. Oxidation may be almost entirely avoided, either by adding the oxide to a mixture of the compound to be alkylated and the alkyl halide, or by adding the substance to a mixture of oxide and halide.

The simplest explanation of the mechanism of the reaction is that the silver oxide serves merely as a means of removing the elements of hydrogen iodide from the sphere of action. That this view is inadequate is shown by the fact that other oxides, such as those of lead, copper, and zinc, are incapable of replacing oxide of silver in the reaction.

The weight of evidence inclines to the view, that the silver oxide acts in virtue of the production of silver derivatives of greater or less stability, which then, by double decomposition with the alkyl iodide, yield the corresponding ethers. According to this view, all the cases of alkylation by this method fall under the second general heading mentioned in the introduction (p. 730). As to the manner in which

the substitution of silver, and eventually alkyl, for hydrogen is brought about, it may certainly be assumed to occur in cases such as those of esters of hydroxy-acids, in virtue of some such preliminary addition of the elements of silver oxide, as that assumed in Walden's explanation of the optical inversion in the conversion of active chlorosuccinic acids into active malic acids (*Ber.*, 1899, 32, 1850). In application to a saturated compound like menthol, recourse would have to be made to the theory of the quadrivalency of oxygen. It seems preferable, however, to regard the reaction in every instance as simply one of double decomposition, the hydrogen atom ultimately replaced by alkyls being first replaced by silver. The cycle of changes involved could then be represented by the equations:  $2\text{ROH} + \text{Ag}_2\text{O} = 2\text{ROAg} + \text{H}_2\text{O}$ ;  $2\text{ROAg} + 2\text{R'I} = 2\text{ROR'} + 2\text{AgI}$ ;  $\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2\text{R'I} = 2\text{R'OH} + 2\text{AgI}$ .

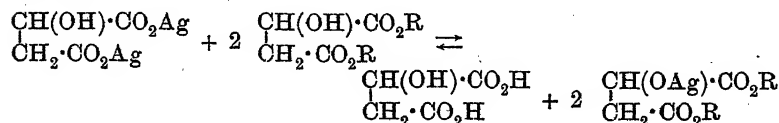
The direct interaction of dry silver oxide and alkyl iodides with formation of ethers represents a process of simple double decomposition,  $\text{Ag}_2\text{O} + 2\text{RI} = \text{R}_2\text{O} + 2\text{AgI}$ , and is comparable with the production, by the action of basic oxides, of diglycollic acid from chloroacetic acid (Schreiber, *J. pr. Chem.*, 1876, [ii], 13, 436), and of ether by the action of sodium oxide upon ethyl iodide (Greene, *Bull. Soc. Chim.*, 1878, [ii], 29, 458). With regard to the cases of ether formation mentioned in the introduction, it must be pointed out that Linne-mann, in the preparation of propyl ether, employed a mixture of propyl iodide, dry silver oxide, and acetic acid, and that Erlenmeyer, in preparing isopropyl ether, used moist silver oxide. Wurtz (*loc. cit.*) states that interaction of dry silver oxide and ethyl or methyl iodides is very energetic, the substances reacting immediately on one another, with great disengagement of heat. In the author's experience, reaction between thoroughly dried oxide and iodide is very tardy. When 23 grams of dry oxide were added to 32 grams of ethyl iodide, the temperature rose momentarily from  $14.5-15^\circ$ , and then sank steadily, remaining in a corked flask at the temperature of the laboratory for many hours. After standing  $3\frac{1}{2}$  days, the liquid was filtered. The liquid consisted mainly of unchanged iodide. The residue, dried at  $100^\circ$ , weighed 29 grams (silver iodide requires 47), indicating that about 25 per cent. of the oxide had entered into reaction. It is probable that interaction with formation of ethers depends upon the presence, or initial formation, of small quantities of alcohol (or water), thus,



The fact that in the presence of a third, more acidic compound the action results in the alkylation of that compound, rather than

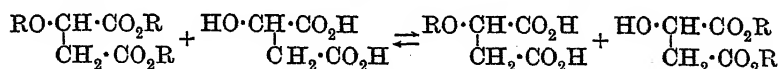
in the production of ether, would follow from the relatively small tendency of the alcohol to form intermediate silver salts.

The formation of unstable silver salts of esters of hydroxy-acids may afford an explanation of the production of esters of alkyloxy-acids in the interaction of silver salts and alkyl iodides (Purdie and Lander, *Trans.*, 1898, 73, 289). We may imagine in this instance that the ester of the hydroxy-acid, in virtue of its feebly acidic character, enters into double decomposition according to the reversible reaction :



The silver compound of the ester would then undergo further reaction with the alkyl iodide, yielding the alkyloxy-ester. The production of alkyloxy-esters in the interaction of iodides and oxy-silver salts is accompanied in all cases by the production of free organic acid, and the amount of alkyloxy-ester produced varies with the amount of free acid obtained. This fact finds ready explanation by the assumption here made. The explanation, it is true, scarcely covers the fact that free alkyloxy-acid is also found, although in very much smaller proportion, along with free hydroxy-acid.

Free alkyloxy-acid might, however, result from the partition of the ethyl group between the free hydroxy-acid and alkyloxy-ester :



or more simply by the partial hydrolysis possibly effected by the dry potassium carbonate, used in the removal of free acid from the product.

It must be pointed out that the greater production of free acid in the action of isopropyl than in that of ethyl iodide, may be due to the decomposition of the iodide  $\text{CH}_3\text{·CHI·CH}_3 = \text{HI} + \text{CH}_3\text{·CH·CH}_3$ . The corresponding reaction with ethyl iodide is not, however, so likely to occur.

If this view of the reactions in question be correct, it might be expected that the formation of esters of alkyloxy-acids could be brought about by the joint action of ethyl iodide and the silver salt of a weak acid on an ester of a hydroxy-acid. As a test case, the action of silver carbonate and ethyl iodide on ethyl tartrate was examined. No action occurred in the cold during one hour with a mixture of 39 grams of silver carbonate, 20 grams of ethyl tartrate, and 44 grams of ethyl iodide. On boiling, a moderately energetic

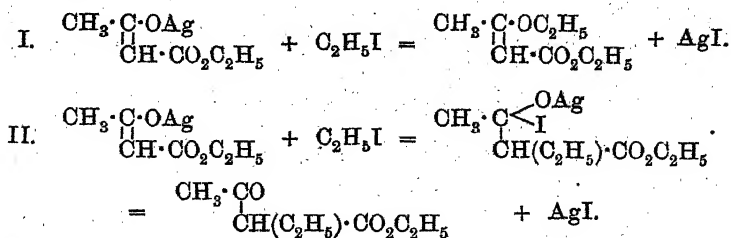
action set in, the yellow silver salt rapidly darkening, and eventually turning black. The product, after 4 hours boiling, was a viscid, neutral liquid. After removal of ethyl carbonate in a vacuum, the bulk of the substance distilled over between  $151^{\circ}$  and  $154^{\circ}$  under 11 mm. pressure. In a 100 mm. tube at  $20^{\circ}$ , the liquid gave  $\alpha_D + 32.02^{\circ}$ . Ethyl tartrate gives at the same temperature  $\alpha_D + 9.13^{\circ}$ , and ethyl diethoxysuccinate at  $18^{\circ}$ ,  $\alpha_D + 97.52^{\circ}$  (Purdie and Pitkeathly, *loc. cit.*, 159). The notable increase in rotation caused by the action of silver carbonate and ethyl iodide is attributable most simply to the formation of roughly 25 per cent. of dialkyloxy-ester.

A mixture of silver acetate, ethyl tartrate, and excess of ethyl iodide was similarly boiled for 3 hours. Free acid resulted as one of the products, and was removed by potassium carbonate. About one-half of the neutral product consisted of unchanged ethyl tartrate ( $\alpha_D^{20^{\circ}} + 9.25^{\circ}$ ); the remainder was a thick, tarry mass, which could not be distilled in a vacuum. Apart from the small likelihood of partition of silver occurring between a strong acid, such as acetic, and a hydroxy-ester, the fact that the reaction apparently pursued a different course from that anticipated renders the result of the experiment inconclusive.

The results obtained with ethyl acetoacetate are of interest with respect to the question of the probable constitution of this substance. Physical considerations are regarded as proving that ethyl acetoacetate consists mainly of the ketonic form, mixed, however, with a small proportion of the enolic form, the substance presenting an instance of equilibrium of the unimolecular type, as suggested by Traube (*Ber.*, 1896, 29, 1715). The failure of chemical methods of proof of the presence of the two dynamic isomerides in ethyl acetoacetate is attributable in great measure to the fact that a substituting agent usually acts exclusively with one or the other form, as is well shown in the case of diazomethane (von Pechmann, *loc. cit.*). In this particular instance, the equilibrium law would lead us to expect that, as soon as the enolic form has been rendered stable by conversion into methoxycrotonate, more of the enolic form will be produced from the ketonic form, in quantity depending upon the coefficients of velocity of the two isomeric changes, until eventually the whole of the substance has reacted in the enolic form. Such considerations (compare Lowry, *Trans.*, 1899, 75, 241) serve to account for the influence of the so-called ketonising and enolising agents in determining in which form condensation with benzalaniline shall ensue (Schiff, *Ber.*, 1898, 31, 207, 601). Similarly, in the interaction of ethyl acetoacetate with ethyl orthoformate, even although some proportion of the substance were initially present in the hydroxy-form, in so far as the orthoformate appears capable of reaction only with the ketonic form

(Claisen, *Ber.*, 1896, 29, 1005), eventually the whole of the acetoacetate will have reacted in the latter form. Granting that alkylation by means of silver oxide and iodides depends upon the preliminary formation of silver substitution compounds of types corresponding to those of the alkyl derivatives eventually obtained, the simultaneous production from ethyl acetoacetate of both  $\text{O}\cdot\text{C}_2\text{H}_5$  and  $\text{C}\cdot\text{C}_2\text{H}_5$  homologues, points to the prior formation of the two silver salts,  $\text{CH}_3\cdot\text{C}(\text{OAg})\cdot\text{CH}\cdot\text{CO}_2\text{C}_2\text{H}_5$  and  $\text{CH}_3\cdot\text{CO}\cdot\text{CHAg}\cdot\text{CO}_2\text{C}_2\text{H}_5$ , and therefore to the existence of both ketonic and enolic forms in the original substance. If the silver oxide is assumed to act merely by elimination of the elements of hydrogen iodide, the conclusion is more direct, or even unavoidable. The elements of hydrogen iodide would be removed from the ethyl iodide and the replaceable hydrogen atom of the two characteristic groupings  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  and  $\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot$ , and the results obtained would therefore indicate the presence of both these groups in ethyl acetoacetate. As stated above, the view that silver derivatives are actually formed is adopted here.

In cases of syntheses effected by the aid of metallo-derivatives, such as the formation of alkyl homologues from ethyl sodioacetoacetate, in so far as only one type of alkyl homologue is produced, it is possible to explain its formation either by the  $\text{ONa}$  or  $\text{CNa}$  constitution for the sodium salt. Where both types of derivative are produced, as, for example, in the action of ethyl chlorocarbonate on ethyl sodioacetoacetate (Claisen, *Ber.*, 1892, 25, 1768), and in the action of acetyl chloride on the sodium and copper compounds (Nef, *Annalen*, 1893, 276, 222), it may be assumed (Nef) that the interaction is of two distinct kinds, namely, double decomposition, and replacement with prior addition. The assumption, certainly by no means improbable, is here made that two definite substances interact, not in one, but in two senses, the course of the reaction of silver oxide and ethyl iodide with ethyl acetoacetate being admittedly susceptible of explanation in the two following ways:



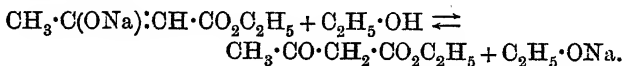
Similar equations would serve to account for the formation of both types of ethyl compound, using the  $\text{CH}_3\cdot\text{CO}\cdot\text{CHAg}\cdot\text{CO}_2\text{C}_2\text{H}_5$  formula, if the elements of  $\text{C}_2\text{H}_5\text{I}$  in the indirect action are assumed to be

added on to the CO group. In conformity with the known tendency on the part of silver to form salts corresponding to the enolic or labile form of tautomeric compounds (for example, benzamide, succinimide), it might be expected that the silver salt of ethyl acetoacetate would possess the OAg structure. As such, since interaction with ethyl iodide results in the formation of the  $\text{O}\cdot\text{C}_2\text{H}_5$  compound in small proportion, it seems difficult to account for the fact that the  $\text{C}\cdot\text{C}_2\text{H}_5$  compound constitutes the main product, unless the simultaneous formation of CAg salt is assumed.

The author has been led to adopt the view that both types of silver salt are capable of formation and interaction simply by double decomposition, not only as affording the simplest explanation of the results obtained, but also because it seems to be in harmony with the state of ethyl acetoacetate as a tautomeric pair in dynamic equilibrium. A somewhat important factor in the consideration of the mechanism of interaction of an agent such as silver oxide and ethyl iodide with a mixture of dynamic isomerides, such as ethyl acetoacetate, is the speed with which the reaction once initiated proceeds. By analogy, it might reasonably be expected that the ease with which oxide of silver interacts with formation of OAg salt would be superior to that with which CAg salt is produced. If the rate of interaction of the ester, oxide, and iodide were slow, time would be allowed for the isomerisation of the ketonic form, so that the reaction would run a course parallel to that with diazomethane. The reaction, on the contrary, is very rapid. Admitting the existence of an affinity between oxide and ether tending to the production of the CAg salt, even were it considerably inferior to that tending to produce the OAg salt, little time is allowed for the ketonic form to undergo the isomerisation necessary for the production of the latter. Traube's observations (*loc. cit.*) of the rate of change of density in solution of ethyl acetoacetate indicate that comparatively large intervals of time are required for the establishment of the condition of equilibrium. That the state of equilibrium is not very greatly affected either by change of temperature or influence of solvent is shown by Perkin's observations of electromagnetic rotation (Trans., 1892, 61, 808), and by Wislicenus' colorimetric results (*Annalen*, 1896, 291, 175; *Ber.*, 1899, 32, 2839).

By inference from the case of silver, provided the view here expressed be accepted, it might be inferred by analogy that the constitution of the sodium, and possibly also potassium, salts of ethyl acetoacetate, should be represented as belonging to the CM type. No stress is laid upon such processes of inference. From the fact that occasionally the sodium salt affords derivatives of both types, it might be argued that sodium salts of both types exist. In the author's opinion, the mode of interaction of the sodio-salt may depend in great

measure upon the mode of its application. Claisen's observation that the interaction of an alcoholic solution of ethyl sodioacetoacetate with ethyl chlorocarbonate leads mainly to the production of ethyl carbonate, suggests the conclusion that the alcoholic solution of sodium salt consists of a mixture in equilibrium of ethyl sodioacetoacetate, alcohol, ethyl acetoacetate, and sodium ethoxide :



In such case, it is not easy to say which form of salt undergoes reaction. Supposing that a CR product should be formed preferentially, temporary formation of ONa salt would account for the ultimate reaction of all the ester in that sense. Nevertheless, it should be mentioned that dry ethyl sodioacetoacetate, although the action of iodine effects the elimination of sodium apparently in the C position, yields both O- and C-derivatives by interaction with ethyl chlorocarbonate, in which case it is also employed in the anhydrous form. A similar case is that of ethyl disodiiodiacetosuccinate, which, by the action of iodine on the dry salt, yields ethyl diacetofumarate (Just, *loc. cit.*; compare Paal and Härtel, *loc. cit.*), and, under similar conditions, gives ethyl bisbenzoyloxycrotonate by the action of benzoyl chloride (Paal and Härtel). The formation of fumarate occurs, however, only to the extent of 5 to 10 per cent. Were a question of constitution under discussion, a complete answer to the question could only be given by accounting for the whole of the sodium salt used.

The author's thanks are due to Prof. Purdie for much valuable advice given during the course of this work.

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ST. ANDREWS.

## LXV.—*Hydrosulphides, Sulphides, and Polysulphides of Potassium and Sodium.\**

By W. POPPLEWELL BLOXAM, B.Sc.

IN a paper entitled "The Sulphides and Polysulphides of Ammonium" (Trans., 1895, 67, 277), the author has given a statement of the results of his work in this field. The study of these compounds was continued after publication of this paper, but, owing to experimental difficulties, it was subsequently decided to abandon the further investi-

\* An abstract of a paper communicated to the Chemical Society on June 1, 1899.

gation of ammonium polysulphides, and to attempt the preparation of those of potassium and sodium.

The method adopted for the preparation of ammonium polysulphides (*loc. cit.*, p. 300, *et seq.*) was applied to polysulphides of potassium and sodium, as it avoided the previous preparation of the monosulphides,  $K_2S$  or  $Na_2S$ . It was found, however, that passage of hydrogen sulphide through a solution of caustic potash or soda in contact with excess of finely powdered sulphur yielded a solution containing both polysulphide and thiosulphate. Moreover, at no observed degree of concentration or of temperature could the formation of thiosulphate be avoided. It was found that, excluding the current of hydrogen sulphide, when finely divided sulphur was digested with solutions of caustic potash and soda respectively, the products were in each case polysulphide and thiosulphate. The difference in the behaviour of sulphur on heating with solutions of caustic potash or soda, on the one hand, and ammonia on the other, seems to demonstrate that the concentrated solution of ammonia (a) at the ordinary pressure and at temperatures up to its boiling point, reacts with regard to sulphur as one of  $NH_3.Aq$ , whilst (b) under pressure it reacts as one of  $NH_4.OH$ , and yields polysulphide and thiosulphate.

Solutions of the normal sulphides of potassium and sodium were therefore prepared. Quantitative and qualitative experiments proved the solutions to be free from excess of hydrogen sulphide, hydrosulphide, or hydroxide. Solutions of each sulphide were warmed with excess of finely powdered sulphur, and deep red polysulphide solutions were obtained. In both cases, however, an evolution of hydrogen sulphide was observed, and as this could not result from the action of sulphur on the monosulphides,  $K_2S$  or  $Na_2S$ , a qualitative analysis (compare *Chem. News*, 1895, 72, 63) was made, and both solutions proved to contain polysulphide and thiosulphate. It follows, therefore, that free caustic alkali is present in aqueous solutions of the monosulphides of potassium and sodium. Neither the analytical results nor the use of cupric sulphate solution (*Trans.*, 1895, 67, 289) gives any indication of the presence of free alkali or of hydrosulphide.

The normal sulphides having failed as sources of polysulphides, attention was now paid to the hydrosulphides. A solution of potassium hydrosulphide was prepared, and it was found that, on digestion with sulphur, hydrogen sulphide was evolved, and a red polysulphide solution obtained entirely free from oxidised sulphur. It is not a matter of indifference, therefore, as has been assumed by all previous workers on this subject, whether the normal sulphide or the hydrosulphide is employed in the preparation of polysulphides. Only when the hydrosulphide is employed is the product free from oxidised sulphur.

The complete paper contains a list of previous authors and the titles



of their papers, the list being arranged in chronological sequence. The following is a brief general criticism of this earlier work :

(a) *Cases where solution of the theoretical amount of sulphur was effected in aqueous solutions of the monosulphides,  $K_2S$  or  $Na_2S$  :*

(i) The authors could in no case have obtained the definite polysulphide desired, for the sulphur added was too small in quantity, no allowance being made for the undetected, but simultaneous, formation of thiosulphate.

(ii) From the mixture of polysulphide and thiosulphate so obtained, they could not have separated pure polysulphide; for although separately the thiosulphates of potassium and sodium may be described as insoluble in alcohol (Corney, "Dictionary of Chemical Solubilities," Inorganic, 475, 476), this is far from being the case when they are mixed with polysulphide. The author has been unable to find any solvent capable of effecting the separation of thiosulphate from polysulphide.

(iii) It is significant that in no single case does an author give details of the yield of polysulphide obtained. If crystalline products were obtained, they must have been mixtures of polysulphides with thiosulphate, from which separation of one component in the pure state is not at present possible. Previous observers, however, do not make mention of any difficulty in obtaining crystals, or of obtaining crystals of doubtful purity. An added element of doubt is the absence of description of the properties of the polysulphides.

(b) *Cases where dry methods of preparation were adopted.* The dry methods employed were still less favourable to success. The final product must always have been a mixture, and invariably have contained oxidised sulphur, in some cases also carbonate, from which separation of the polysulphide is not at present possible.

The critical consideration of the work of authors who claim to have obtained the whole range of polysulphides, and the repetition in many instances of their experiments with negative results, justified the conclusion that up to the date of commencing the present work no single polysulphide of potassium or sodium had been obtained in the pure state. It was clear also that before any attempt could reasonably be made to prepare pure polysulphides, it was absolutely necessary to obtain the various sulphides and hydrosulphides of potassium and sodium, and to investigate their properties both in the solid state and in aqueous solution.

## SULPHIDES AND HYDROSULPHIDES OF POTASSIUM.

*Preparation of Potassium Monosulphide.*

A concentrated aqueous solution of caustic potash was divided into two equal portions, one of which was saturated completely with hydrogen sulphide, and the second portion added to it. On concentration in a vacuum over calcium chloride, small, white, glass-like, tabular crystals were deposited. These did not correspond in appearance with the description of the crystals of  $K_2S, 5H_2O$  given by Schöne (Pogg. Ann., 1867, 131, 380), and on analysis yielded the following results:

$K = 23.34$ ;  $S = 9.85$ ;  $H_2O$  (diff.) = 66.81.

$K_2S, 12H_2O$  requires  $K = 23.92$ ;  $S = 9.82$ ;  $H_2O = 66.26$  per cent.

This hydrate, however, has not been obtained again during the series of experiments. The mother liquor yielded, on further concentration, a large crop of crystals of a different form which, drained free from the red mother liquor, were colourless, brilliant, four-sided, flat rhombs, and very deliquescent in air. On analysis, the following results were obtained:

$K = 38.42$ ;  $S = 15.96$ ;  $H_2O = 45.62$ .

$K_2S, 5H_2O$  requires  $K = 39.00$ ;  $S = 16.00$ ;  $H_2O = 45.00$  per cent.

*Production of Dihydrated Potassium Monosulphide,  $K_2S, 2H_2O$ .*

The clear, glass-like crystals of  $K_2S, 5H_2O$ , when exposed in a vacuum over sulphuric acid, rapidly effloresced, and when powdered repeatedly and exposed over the acid in a vacuum, eventually yielded a product giving concordant analytical results:

$K = 53.20$ ;  $S = 21.52$ ;  $H_2O$  (diff.) = 25.28.

$K_2S, 2H_2O$  requires  $K = 53.42$ ;  $S = 21.91$ ;  $H_2O = 24.67$  per cent.

In appearance, dihydrated potassium monosulphide closely resembles granulated calcium chloride.

*Stability of Potassium Monosulphide towards Heat.*

Crystals of pentahydrated potassium monosulphide,  $K_2S, 5H_2O$ , were placed in a small fractional distillation flask and subjected to the action of heat. The salt melted at about  $60^\circ$ , and heating was continued until tranquil fusion was attained. The final temperature reached was beyond the range of the nitrogen mercury thermometer employed ( $560^\circ$ ). Only a trace of hydrogen sulphide was evolved

throughout the process. On cooling, the fused mass was red and deliquesced freely. It proved to be free from both polysulphide and oxidised sulphur; it also reacted with cupric sulphate solution as the monosulphide. Potassium monosulphide, therefore, is stable at a low red heat.

This degree of resistance to decomposition on heating, together with the observed action that sulphur, when gently warmed with the crystals, forms polysulphide and thiosulphate, suggested that the crystals might be tetrahydrated potassium hydroxyhydrosulphide,  $\text{KHS}, \text{KOH}, 4\text{H}_2\text{O}$ .\* Such a compound would reasonably be expected to be stable at a high temperature, and its observed behaviour with sulphur would also be intelligible. Distinction between the compounds  $\text{K}_2\text{S}, 5\text{H}_2\text{O}$  and  $\text{KSH}, \text{KOH}, 4\text{H}_2\text{O}$  could not be effected by the use of reagents, but could be drawn by determining the quantity of water expelled from the salt on heating.

The crystals heated in a current of dried hydrogen lost 45·10 per cent. of water, as against 45·0 per cent. required for  $\text{K}_2\text{S}, 5\text{H}_2\text{O}$ . They consisted, therefore, of pentahydrated potassium monosulphide.

#### *Attempts to Prepare Potassium Hydrosulphide in the Dry Way.*

Unsuccessful attempts have been made by Baur (*J. pr. Chem.*, 1858, 75, 246) and Sabatier (*Ann. Chim. Phys.*, 1881, [v], 22, 1) by the action of dry hydrogen sulphide on heated potassium carbonate. The present author failed to obtain it by passing hydrogen sulphide through molten potassium carbonate. The product had the composition  $4\text{KHS}, \text{K}_2\text{S}$ , and, notwithstanding the prolonged passage of the gas through the molten material, 3·8 per cent. of potassium carbonate was still left undecomposed. Attempts to prepare potassium hydrosulphide,  $\text{KHS}$ , by the action of hydrogen sulphide on fused potassium hydroxide do not seem to have been made previously. Retorts of special Jena glass were obtained, provided with a tube ground in at a right angle to serve as inlet for the gas, and proved sufficiently resistant to the action of alkali. As a result, admixtures of sulphide and hydrosulphide were obtained—for example,  $\text{K}_2\text{S}, \text{KHS}$  and  $3\text{K}_2\text{S}, \text{KHS}$ , but the author failed to obtain potassium hydrosulphide. The preparation of anhydrous potassium hydrosulphide therefore does not seem to be practicable in the dry way.

#### *Preparation of Hemihydrated Potassium Hydrosulphide.*

Two hundred grams of caustic potash were covered with 100 grams of water, and the temperature raised to 90°. Saturation with hydrogen sulphide was effected at this temperature, the gas being rapidly

\* Compare  $\text{Ca}(\text{SH})\text{OH}$ , described by Divers and Shimidzu (*Trans.*, 1884, 45, 270).

absorbed and the hydroxide passed completely into solution. On cooling, a few cubic centimetres of a strong solution of potassium hydroxide were added to the solution placed in a wide-mouth stoppered bottle, the stopper replaced, and the bottle and its contents shaken. In this way, any free hydrogen sulphide was removed. Precipitation of iron sulphide, &c., was observed, and, on filtration through a cotton-wool plug, a perfectly bright, brownish-yellow solution was obtained. On concentration in a vacuum over sulphuric acid, a crop of fine, dust-like crystals separated, which resembled those of ammonium chloride rapidly deposited from a concentrated solution. The salt is very deliquescent, rendering it most difficult to isolate a satisfactory product for analysis. The following results were obtained on analysis:

$K = 49.78$ ;  $S = 39.29$ ;  $H_2O + H$  (diff.)  $= 10.93$ .  
 $KHS, \frac{1}{2}H_2O$  requires  $K = 48.15$ ;  $S = 39.51$ ;  $H_2O + H = 12.34$  per cent.

*Preparation of Anhydrous Potassium Hydrosulphide.*

The method of preparation here employed was suggested to me by Dr. Scott, who had prepared anhydrous sodium hydrosulphide in a similar fashion. In outline, it consists in passing hydrogen sulphide through rectified ether,\* in which is placed metallic potassium. Hydrogen is rapidly evolved from the surface of the metal, which remains quite bright throughout the operation, and potassium hydrosulphide separates as a snow-white powder. The product is washed with rectified ether, and on drying in a vacuum over sulphuric acid, is obtained as a very slightly yellow, dust-like, crystalline powder, deliquescent with extreme rapidity on exposure to air. As the result of several analyses:

$K$  (mean value)  $= 53.49$ .  $KHS$  requires  $K = 54.17$  per cent.

This method of preparation of potassium hydrosulphide is much more rapid and convenient than that employed by Sabatier (*loc. cit.*), who dehydrated the crystalline hydrosulphide by heating the crystals in a current of dry hydrogen sulphide.

*Stability of Potassium Hydrosulphide towards Heat.*

The method employed was similar to that used in the case of potassium monosulphide (p. 756), with the exceptions that the fractional distillation flask was heated in a bath of melted solder, and that the bulb of the nitrogen mercury thermometer was placed in a protective tube of Jena glass immersed in the melted solder. At

\* If ether containing alcohol be employed, the product will be contaminated with oxidation products of potassium ethoxide.

450°, fusion was observed at the edges of the crystals, and at 510° was complete and tranquil. Heating was continued to the upper limit of the thermometer, 560°, but no evolution of gas was observed. Thus the change expressed by the equation  $2\text{KHS} = \text{K}_2\text{S} + \text{H}_2\text{S}$  is not effected at temperatures below 560°. Potassium hydrosulphide is therefore stable on exposure to heat, and, in this respect, will bear comparison with its oxygen analogue KOH. The melting point of the hydrosulphide was next determined, employing a nitrogen mercury thermometer, previously standardised in the vapour of boiling sulphur, and as a mean of three determinations was found to be 455°.

*Stability of  $\text{K}_2\text{S}, 5\text{H}_2\text{O}$  and  $\text{KHS}, \frac{1}{2}\text{H}_2\text{O}$  on Exposure to Air.*

Previous observers unite in regarding these salts as unstable, and therefore to be preserved from contact with the air. In the progress of the present work, the following facts were established. Both salts are, it is true, exceedingly deliquescent, but if exposed to air, free from carbon dioxide, they do not evolve hydrogen sulphide. Carbon dioxide acts rapidly on the salts or their aqueous solutions, with evolution of hydrogen sulphide and formation of the corresponding carbonates. Experiments were also made to determine whether these salts were affected by moist oxygen free from carbon dioxide. As a result, very slight absorption of oxygen was observed with each. In both cases, the salts remained quite white, no polysulphide being formed.

In the case of the pentahydrate,  $\text{K}_2\text{S}, 5\text{H}_2\text{O}$ , the main product of oxidation was sulphite; no thiosulphate could be detected, and a trace only of sulphate. In the case of the hemihydrate,  $\text{KHS}, \frac{1}{2}\text{H}_2\text{O}$ , however, the main product of oxidation was found to be thiosulphate; no sulphate could be detected, and a trace only of sulphite. Similar results were obtained by slowly passing a stream of oxygen, free from carbon dioxide, through aqueous solutions of each salt. These results are in opposition to the current statements that, on exposure of these salts, or their solutions, to air, polysulphides are formed and hydrogen sulphide is evolved: statements which are true only if the air contains carbon dioxide.

*Change effected on boiling Aqueous Solutions of Potassium Sulphide and Hydrosulphide.*

Several conflicting statements are to be found on this subject. Of earlier observers, Gay Lussac and Berzelius (*Ann. Chim. Phys.*, 1821, 20, 34) believe that solutions of potassium hydrosulphide do not decompose on boiling. Berzelius, in fact, recommends boiling, to free the solution of hydrosulphide from excess of hydrogen sulphide, and according to him, solution of potassium hydrosulphide can be evapor-

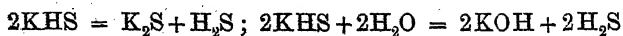
ated without decomposition. Thénard, on the other hand, asserts (*Ann. de Chimie*, 1812, 83, 133) that the hydrosulphide decomposes on boiling. Schöne states (*loc. cit.*) that after boiling a solution of potassium hydrosulphide for  $1\frac{1}{2}$  hours, it is for the most part decomposed into monosulphide, and regards it as possible that in this way, not only is monosulphide formed, but that the decomposition goes further. Solutions of the so-called monosulphide lose hydrogen sulphide continually on boiling, although only very slowly and with difficulty, so that, according to Schöne, the conclusion may be drawn that on continuing the boiling long enough, all hydrosulphide, monosulphide, or hydroxyhydrosulphide would be transformed into hydroxide.

To test these various and conflicting statements, aqueous solutions of the sulphide and hydrosulphide, of 20 per cent. concentration, were boiled, in the first instance, in air, but later, in a current of hydrogen, to eliminate the influence of the action of the air. Twenty per cent. solutions were employed in order that the results might be compared with those previously obtained by Walker (*Proc. Roy. Soc. Edin.*, 1894, 20, 255).

On boiling a 20 per cent. solution of the pentahydrate,  $K_2S \cdot 5H_2O$ , for  $2\frac{1}{2}$  hours in contact with air, the evolution of hydrogen sulphide was negligible, and the solution contained only traces of polysulphide and sulphite and very little more thiosulphate. A similar solution, boiled for  $1\frac{1}{2}$  hours, while hydrogen was led through it, evolved only a trace of hydrogen sulphide. Thus Schöne's statement is incorrect, and the stability, on boiling, of a 20 per cent. aqueous solution of this hydrate is established.

In similar fashion, a 20 per cent. solution of  $KHS \cdot \frac{1}{2}H_2O$  was boiled. The solution contained 18.1236 grams of crystals dissolved in 72.49 grams of water, and was boiled vigorously for  $1\frac{1}{2}$  hours in a current of hydrogen, the escaping gas being led through copper sulphate solution. The amount of sulphuric acid liberated was 0.231 gram, equivalent to 0.080 gram of hydrogen sulphide, and corresponds to a destruction of 0.191 gram of  $KHS \cdot \frac{1}{2}H_2O$ , or of 1.05 per cent. of the total salt present. The result of this experiment is opposed to the experience of Schöne, who found that a solution of potassium hydrosulphide (of which the concentration is not stated), after boiling for  $1\frac{1}{2}$  hours, is for the most part decomposed into monosulphide.

It follows, then, that although a solution of potassium hydrosulphide is not so stable on boiling as one of potassium sulphide of the same concentration, the rate of change on boiling is very slow, and that neither of the equations



put forward as expressing its mode of decomposition under these conditions can be accepted.

#### SULPHIDES AND HYDROSULPHIDES OF SODIUM.

A considerable amount of work has been published on these compounds by Berthier (*Ann. Chim. Phys.*, 1822, 22, 225), Kircher (*Annalen*, 1839, 31, 339), Finger (*Pogg. Ann.*, 1866, 128, 635), Sabatier (*loc. cit.*) and others, but from the present summary a criticism of the results obtained by these authors is excluded for the sake of brevity.

##### *Preparation of Sodium Monosulphide, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ .*

This preparation was effected, on the lines recommended by Finger and by Sabatier, by saturating a concentrated solution of caustic soda with hydrogen sulphide. One hundred grams of caustic soda (prepared from sodium) were dissolved in 100 grams of water. On passing hydrogen sulphide into the solution, needle-like crystals were deposited in considerable quantity (compare Finger and Sabatier). These could not be hydrosulphide, as the quantity of gas which had passed into the solution was altogether insufficient. Further, if the crystals were those of hydrosulphide, it would be necessary to assume :—(a) that it is the first product of the reaction, (b) that it is practically insoluble in solution of caustic soda. The crystals might be those of hydrated sodium monosulphide (compare Finger and Sabatier) or might have the composition  $\text{Na}_2\text{S}\cdot x\text{NaOH}$ . On continuing the current of gas, the crystals dissolved before saturation was complete; thus it seems probable that they are of the latter type, and it is noteworthy that subsequently (p. 764) crystalline substances of this character were isolated. The flask and its contents were left undisturbed for three days, when large, colourless, octahedral crystals were deposited. Some of these were examined and found to consist of the enneahydrate  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (compare Finger and Sabatier). Solution of the main portion of the crystals was now attempted by addition of hot water and application of heat. Two kinds of crystals were observed to be present during the progress of solution (compare Finger and Sabatier). Through the hot liquid still containing crystals, hydrogen sulphide was passed, until solution was complete and the gas ceased to be absorbed. To the solution, which was now presumably one of sodium hydrosulphide, was added 100 grams of powdered caustic soda, which dissolved with considerable evolution of heat, and when cold the whole was concentrated over sulphuric acid under 15 mm. pressure. Crystallisation, from a supersaturated solution, occurred during the night, particles being projected on to the glass bell jar. Solution was again effected by addition of small quantities of

hot water. On further concentration over sulphuric acid under 15 mm. pressure, no crystals were obtained during 24 hours. Air was therefore admitted to the receiver and some of the solution withdrawn in a pipette. On transference to a test tube, crystallisation took place and some of the crystals were used as nuclei for the main solution. Rapid crystallisation followed, in radiate masses of prismatic forms, altogether unlike the octahedra previously obtained. Analysis of these crystals gave the following results:

Na = 18.89; S = 12.99;  $H_2O$  (diff.) = 68.12.

$Na_2S \cdot 9H_2O$  requires Na = 19.16; S = 13.33;  $H_2O$  = 67.51 per cent.

The crystals were accepted as another form of the enneahydrate, and on keeping them under the mother liquor they changed into the ordinary form of octahedra. Finger and Sabatier obtained crystals, under similar experimental conditions, undergoing transformation into the stable octahedra. To these, the following formulæ were given:  $Na_2S \cdot 5H_2O$  (Sabatier), and  $Na_2S \cdot 6H_2O$  (Finger). It is possible that a series of unstable lower hydrates of sodium monosulphide may exist, all passing into the stable octahedral form by further hydration. The author has not obtained either of these hydrates, and, but for the analytical data, given by Sabatier and Finger, would be of opinion that the unstable salt had, in all cases, the composition  $Na_2S \cdot 9H_2O$ .

#### *Stability of $Na_2S \cdot 9H_2O$ and its Aqueous Solutions.*

The author finds himself in agreement with Walker (*loc. cit.*), who states that the crystals of  $Na_2S \cdot 9H_2O$  do not evolve hydrogen sulphide in air free from acid, and that, at the ordinary temperature, a solution of sodium monosulphide does not smell of this gas. The account of Walker's experiments with a 20 per cent. solution of this hydrate, boiled in a current of hydrogen, is not accompanied by figures to show the loss of hydrogen sulphide.

The following are the figures obtained by the author. 17.459 grams of  $Na_2S \cdot 9H_2O$  were dissolved in 69.84 grams of water. In the cold, a current of hydrogen did not carry off hydrogen sulphide from the solution, and on boiling for 25 minutes only a trace of copper sulphide was deposited. The acid so liberated from copper sulphate solution amounted to 0.0318 gram  $H_2SO_4$  = 0.011 gram  $H_2S$ , indicating that 0.435 per cent. of  $Na_2S \cdot 9H_2O$  had been decomposed. The salt is then slightly less stable than one of  $K_2S \cdot 5H_2O$ , under the same conditions (p. 756).

From the observed rate of decomposition of a 20 per cent. solution of  $Na_2S \cdot 9H_2O$ , it would be necessary to boil it for an infinitely long



period in a current of hydrogen to completely decompose it in the sense:  $\text{Na}_2\text{S} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2\text{S}$ .

*Attempts to prepare Sodium Hydrosulphide.*

Sabatier (*loc. cit.*) claimed to have prepared the hydrosulphide  $\text{NaHS}$  by acting on crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  with hydrogen sulphide, but the author, following his process, has failed to obtain it. The crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  do not absorb hydrogen sulphide at all rapidly, even when finely powdered and agitated with the gas, and progressive dilution with small quantities of water does not ensure its absorption. The behaviour of the crystals is comparable with that of the compound  $(\text{NH}_4)_2\text{S} \cdot 2\text{NH}_4\text{HS}$  in similar circumstances (*Trans.*, 1895, 67, 284).

When about four volumes of solution were present for one volume of the original crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  the gas current was maintained for 4 hours and an examination made of the product obtained. On concentration over sulphuric acid in a vacuum, plate-like crystals were deposited, which resembled in general appearance the crystals of  $(\text{NH}_4)_2\text{S} \cdot 2\text{NH}_4\text{HS}$ , previously referred to. On analysis, the following results were obtained:

$\text{Na} = 26.20$ ;  $\text{S} = 19.17$ .  $\text{NaHS}$  ( $\text{Na} = 26.20$  per cent.) requires  $\text{S} = 36.41$ .  $\text{Na}_2\text{S}$  ( $\text{Na} = 26.20$  per cent.) requires  $\text{S} = 18.23$ .

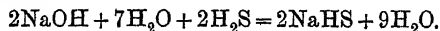
The salt has approximately the composition  $\text{Na}_2\text{S}$ , but, by its action on cupric sulphate solution, is found to contain some hydrosulphide, 2.32 per cent. of the total sulphur being present in this form. The proportions correspond to those required for a compound  $7\text{Na}_2\text{S} \cdot \text{NaHS} \cdot 40\text{H}_2\text{O}$ , which requires  $\text{Na} = 26.09$ ;  $\text{S} = 19.36$ ;  $\text{H} = 0.07$ ;  $\text{H}_2\text{O} = 54.48$  per cent. The failure of crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  to take up hydrogen sulphide to form  $2\text{NaHS}$ , and the similar failure, even in the case of aqueous solutions of sodium monosulphide,  $\text{Na}_2\text{S}$ , taken together with the formation of intermediate products observed during saturation of aqueous solutions of caustic soda with hydrogen sulphide, bear a considerable resemblance to the phenomena observed when ammonia solution is saturated with hydrogen sulphide. This observation is the more remarkable, for nothing of the kind was noticed during the saturation of solutions of caustic potash with the gas.

As the system  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , in the solid state, and at the temperature of the air, is proof against attack by hydrogen sulphide, and as only a very small proportion of  $\text{NaHS}$  was formed at the ordinary temperature on increasing the amount of water very considerably, experiments were now made to test the effect of increase of temperature on the absorption of the gas. The crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  commenced to melt when heated to  $53^\circ$  and were completely fused at  $80^\circ$ . The substance so melted was kept at  $85^\circ$  and saturated with hydrogen sulphide. The

relation Na/S, determined in the solution, was found to be that required by NaHS, the figures showing only a slight deficiency of 0.19 per cent. of sulphur.

*Action of Hydrogen Sulphide on a Solution of approximately the Composition  $2\text{NaOH}, 7\text{H}_2\text{O}$ , kept at  $0^\circ$ .*

The strength of the solution of caustic soda was suggested by the consideration that a solution of the concentration  $\text{Na}_2\text{S}, 9\text{H}_2\text{O}$ , maintained at  $85^\circ$ , takes up hydrogen sulphide in accordance with the equation  $\text{Na}_2\text{S}, 9\text{H}_2\text{O} + \text{H}_2\text{S} = 2\text{NaHS} + 9\text{H}_2\text{O}$ . Proceeding from a solution of caustic soda to one of sodium hydrosulphide, we have the following relation :



A solution of the composition  $2\text{NaOH} + 7\text{H}_2\text{O}$  would contain 38.83 per cent. of caustic soda ; that employed contained 36.91 per cent. From the first, on passing the gas, plate-like crystals were deposited, and their formation continued until a semi-solid mass was obtained. The current of gas was continued until saturation was effected, but the crystals did not dissolve. After separation from the mother liquor, they dissolved readily in water, did not smell of  $\text{H}_2\text{S}$ , and, on testing with solution of cupric sulphate gave a filtrate which was free from acid, whilst the precipitate contained cupric hydrate,  $\text{Cu}(\text{OH})_2$ . The crystals therefore contain free NaOH, and must be of the type  $\text{NaOH}, \text{NaHS}, x\text{NaOH}$  or  $\text{Na}_2\text{S}, x\text{NaOH}$ . The main portion of crystals was dissolved in water, and the solution, on analysis, gave numbers which showed :

(i) That there was not sufficient sulphur present for the formation of sodium monosulphide,  $\text{Na}_2\text{S}$ .

(ii) That of the total sodium, 79.60 per cent. was present as sodium monosulphide, and 20.40 per cent. as caustic soda.

From these figures are obtained the empirical numbers 1.730/0.887, or, in whole numbers, 2/1. The constitution of the crystals is then  $(\text{Na}_2\text{S})_{2x}(\text{NaOH})_x$ , of which the simplest expression is  $2\text{Na}_2\text{S}, \text{NaOH}$ .

As the result of the foregoing experiments, it follows that, if sodium hydrosulphide could be obtained at all by direct saturation of solutions of caustic soda with hydrogen sulphide, the solution must be dilute and saturation effected in a hot solution.

*Preparation of Sodium Hydrosulphide by Saturation of Solution of Sodium Hydroxide containing 27.82 per cent. of NaOH with Hydrogen Sulphide at  $100^\circ$ .*

This strength of solution was selected as being within the limits of  $2\text{NaOH}, 9\text{H}_2\text{O}$ , which would contain 33.04 per cent. of NaOH. The

gas was rapidly and completely absorbed, and no deposition of crystals was observed. Analysis of the saturated product showed it to be one of sodium hydrosulphide.

Na = 12.91 ; S = 17.84 per cent.

NaHS requires S = 17.94 for Na = 12.91 per cent.

From this solution, on concentration in a vacuum over sulphuric acid, brilliant, prismatic crystals were obtained, which, on analysis, gave the following results :

Na = 24.88 ; S = 34.01 ; H = 1.07 ;  $H_2O$  = 40.04.

NaHS, 2 $H_2O$  requires Na = 25.00 ; S = 34.78 ; H = 1.09 ;  $H_2O$  = 39.13 per cent.

Dihydrated sodium hydrosulphide is stated to have been obtained previously by Sabatier (*loc. cit.*). On keeping the prismatic crystals under their mother liquor, they are transformed into large, colourless, lustrous rhombs. The results of analysis showed that the crystals were those of a trihydrate.

Na = 20.59 ; S = 29.15 ; H = 0.89 ;  $H_2O$  = 49.37.

NaHS, 3 $H_2O$  requires Na = 20.90 ; S = 29.09 ; H = 0.92 ;  $H_2O$  = 49.09 per cent.

Of the two crystalline hydrosulphides, the trihydrated salt is to be regarded as the more stable form.

Experiments were made on the stability of crystals of NaHS, 3 $H_2O$  with regard to heat and on the stability of aqueous solutions of sodium hydrosulphide, with results which may be briefly described. Trihydrated sodium hydrosulphide melts at 22°, and when heated at 360° loses 20.53 per cent. of its sulphur. Experiments were made with 20 per cent. aqueous solutions in the manner described for potassium hydrosulphide (p. 760), and it was found that the sodium compound is the less stable, although it is not true, as has been repeatedly stated, that a solution of sodium hydrosulphide, on boiling, becomes converted into one of the monosulphide,  $Na_2S$ .

#### CONSTITUTION OF AQUEOUS SOLUTIONS OF THE SULPHIDES AND HYDROSULPHIDES OF POTASSIUM AND SODIUM.

It has been already stated (p. 754) that, as a source of polysulphides it is not a matter of indifference whether a solution of normal sulphide or of a hydrosulphide be used as a solvent for sulphur. Sulphur by its action reveals a vital distinction existing between the two solutions, as in the first case polysulphide and thiosulphate are formed, in the second case polysulphide only. This fact had not been recognised by any previous workers on polysulphides, and in consequence their procedure

was faulty (p. 755). It is sufficient to say that the action of sulphur on aqueous solutions of sulphides and hydrosulphides of potassium and sodium is due to the fact that, whilst the normal sulphide becomes, as a result of hydrolysis, a mixed solution of hydrosulphide and hydroxide, the hydrosulphide exists in solution unaltered (Walker, *loc. cit.*). From these considerations, it follows that, as sources of polysulphides, aqueous solutions of normal sulphides of potassium or sodium are altogether unsuitable, and that the only source of polysulphide available at present is the solid hydrosulphide or its solution.

*Attempted Preparation of Polysulphides of Sodium.*

Attempts were made to obtain the various disodium polysulphides reputed to exist, namely,  $\text{Na}_2\text{S}_2$ ;  $\text{Na}_2\text{S}_3$ ;  $\text{Na}_2\text{S}_4$ ;  $\text{Na}_2\text{S}_5$ . In no case, however, was any product obtained corresponding to these salts, when the calculated amounts of sulphur were dissolved in solutions of sodium hydrosulphide, under the influence of heat and during the passage of a current of hydrogen sulphide. In one case only was a positive result obtained and under the following experimental conditions,\* the object being to prepare disodium pentasulphide.

One hundred grams of a solution of sodium hydrosulphide (containing 20.6 per cent. of sulphur) were treated with 41.2 grams of sulphur, being the theoretical amount necessary for the reaction:  $2\text{NaHS} + \text{S}_4 = \text{Na}_2\text{S}_5 + \text{H}_2\text{S}$ . On heating, nearly all the sulphur was dissolved, but on cooling a large quantity separated. This was removed by filtration from the viscous liquid, which, on standing, did not yield crystals. On analysis of the solution, the following results were obtained, indicating that it is one of tetrasodium enneasulphide,  $\text{Na}_4\text{S}_9$ .

$\text{Na} = 11.82$ ;  $\text{S (total)} = 36.48$ ;  $\text{S (polysulphide)} = 27.65$  per cent.

Taking the total sulphur found, 36.48 per cent. as the basis of calculation,

$\text{Na}_4\text{S}_9$  requires  $\text{Na} = 11.65$ ;  $\text{S (polysulphide)} = 28.35$  per cent.

The solution, when cooled to  $-22^\circ$  by immersion of the flask in a freezing mixture, gave no crystals. It was therefore further concentrated by heating in a current of hydrogen sulphide, and on cooling, crystals were obtained which, on analysis, yielded the following results:

$\text{Na} = 14.64$ ;  $\text{S (total)} = 45.18$ ;  $\text{S (polysulphide)} = 34.71$ ;  $\text{H}_2\text{O} = 40.18$  per cent.

$\text{Na}_4\text{S}_9, 14\text{H}_2\text{O}$  requires  $\text{Na} = 14.55$ ;  $\text{S (total)} = 45.56$ ;  $\text{S (polysulphide)} = 35.44$ ;  $\text{H}_2\text{O} = 39.89$  per cent.

\* The paper by Locke and Austell (*Amer. Chem. J.*, 1898, 20, 592) appeared subsequently to the completion of this portion of the work.

This compound for the present stands alone, the author having failed to obtain any other polysulphides of sodium, a result which is remarkable, as the method employed in the case of potassium hydrosulphide yielded a series of polysulphides.

It is to be noted that the salt obtained is analogous to the ammonium polysulphide,  $(\text{NH}_4)_4\text{S}_9$ , obtained previously. Also that the formula cannot correctly be written on the type of a disodium polysulphide, for the sulphur relations existing in the salt are expressed by  $\text{Na}_4\text{S}_2\cdot\text{S}_7$ .

*Preparation of Potassium Polysulphides.*

These preparations were made by acting on solutions of potassium hydrosulphide with sulphur. Two distinct series of experiments were conducted.

*Series I*, in which sulphur, in calculated quantity, was digested with solution of potassium hydrosulphide, and hydrogen sulphide passed through the hot solution, concentration being effected by boiling in a current of the gas.

*Series II*, in which sulphur, in calculated quantity, was digested with solution of potassium hydrosulphide, concentration being effected in a vacuum over sulphuric acid.

The results of both series of experiments are given in the table (p. 768). In the left hand column are found the formulæ of the products obtained,\* arranged in order of their sulphur values, commencing with  $\text{K}_4\text{S}_{10}$  and ending with  $\text{K}_4\text{S}_6$ .

Reference to the middle column will reveal the object with which the experiment was made, and furthermore, whether the experiment belongs to Series I or II.

The following remarks are made on the results of experiments grouped together in the table.

(1) The highest product obtained by direct solution of sulphur in potassium hydrosulphide is  $\text{K}_4\text{S}_9$ , and of this both a solution and crystals are obtained (see  $\beta$  and  $\gamma$ ). Sufficient sulphur is taken up on heating to form  $\text{K}_4\text{S}_{10}$ , but some is deposited on cooling, leaving a stable solution of  $\text{K}_4\text{S}_9$  (see  $\beta$ ).

(2) If, however, concentration of a hot solution of  $\text{K}_4\text{S}_9$  is effected

\* The old conception of diammonium, disodium, and dipotassium polysulphides is abandoned, and all the polysulphides are held to be of the same character, namely, tetrammonium, tetrasodium, or tetrapotassium compounds. This step is, in the author's opinion, rendered necessary by the existence of certain definite polysulphides, whose composition cannot be expressed by formulæ written on the type  $\text{M}'_2\text{S}_x$ . Thus, we have representatives of this class in the case of all three metals:  $(\text{NH}_4)_4\text{S}_7$  and  $(\text{NH}_4)_4\text{S}_9$ ,  $\text{Na}_4\text{S}_9$ , and  $\text{K}_4\text{S}_7$  and  $\text{K}_4\text{S}_9$ .

Expt.	Sulphides obtained.	Object and method of experiment.	Remarks.
(a).....	$K_4S_{10}, xH_2O$	KHS + S (excess). I. Concentration in current of $H_2S$ .	A solution of $K_4S_{10}$ obtained, and from it crystals of $K_4S_{10}, xH_2O$ .
(b).....	$K_4S_9, xH_2O$	KHS + S (for $K_4S_{10}$ ). II. No current of $H_2S$ .	All sulphur dissolved on heating, but deposition of sulphur on cooling. Solution of $K_4S_9$ , and crystals of $K_4S_9, xH_2O$ , from it.
(c).....	$K_4S_9, xH_2O$	KHS + S (excess over requirements of $K_4S_{10}$ ). II. No current of $H_2S$ .	Crystals of $K_4S_9, xH_2O$ , admixed with sulphur. On exhaustion with carbon disulphide $K_4C_9, xH_2O$ , yielded $K_4S_9, 10H_2O$ .
(d).....	$K_4S_8, 6H_2O$	KHS + S (for $K_4S_8$ ). II. No current of $H_2S$ .	Only 50 per cent. of KHS active. $K_4S_8$ yields $K_4S_8$ on treatment with $CS_2$ .
(e).....	$K_4S_8, 6H_2O$ $K_4S_8, 19H_2O$	KHS + S (for $K_4S_8$ ). I. Concentration in current of $H_2S$ .	$K_4S_8, 6H_2O$ , yields, on recrystallisation from alcohol, $K_4S_8, 19H_2O$ .
(f).....	$K_4S_7$ (approx.)	KHS + S (for $K_4S_8$ ). I. Concentration in current of $H_2S$ .	Product obtained higher than that for which sulphur added was sufficient.
(g).....	$K_4S_6$ (approx.)	KHS + S (for $K_4S_8$ ). I. Concentration in current of $H_2S$ .	Product obtained higher than that for which sulphur added was sufficient.

by passage of hydrogen sulphide, then a solution of  $K_4S_{10}$  is obtained, and from it crystals of  $K_4S_{10}, xH_2O$ , (see a).

Here some explanation seems to be required to account for the formation of a higher polysulphide than can be obtained by direct solution of sulphur in potassium hydrosulphide. It has been repeatedly observed that hydrogen sulphide rapidly decomposes polysulphides, if passed through a *cold* solution, sulphur being copiously deposited and potassium hydrosulphide formed. If, however, hydrogen sulphide is passed through a *hot* solution of a polysulphide, no deposition of sulphur is observed, but the depth of colour is increased. The necessary explanation may be found in these facts, and it is suggested that, in the experiments *a* under consideration, some

potassium hydrosulphide is formed on passage of hydrogen sulphide through a *hot* solution of  $K_4S_9$ , and that the liberated sulphur, at the moment of its separation, is taken up by unaltered  $K_4S_9$ , forming the higher compound  $K_4S_{10}$ .

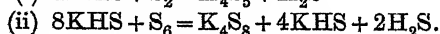
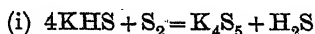
(3) It is to be noted that in all cases the polysulphide obtained is *richer* in sulphur than that for which the sulphur added was sufficient. This requires elucidation and two suggestions are made :

(a) All the sulphur added unites selectively with a *portion* only of the potassium hydrosulphide, forming a higher polysulphide than was designed in the experiment, and leaving potassium hydrosulphide in solution unaltered.

(b) That the formation of the higher polysulphide is due to the action of the current of hydrogen sulphide on the polysulphide first formed (see paragraph 2).

(4) It is evident on considering the results of experiments  $\alpha$ ,  $\epsilon$ ,  $\xi$ ,  $\eta$  (Series I), that it is not possible to discriminate between (a) the first product obtained on dissolving sulphur in potassium hydrosulphide, and (b) the condensing effect of the current of hydrogen sulphide on the polysulphide first formed.

(5) Attention may now be directed to the experiments of Series II, (see  $\beta$ ,  $\gamma$ ,  $\delta$ ), in which no current of hydrogen sulphide was employed. Turning to the experiment marked  $\delta$  in the Table, the intention was to produce  $K_4S_5$ , for which the sulphur added was sufficient. As a matter of fact, *the product obtained was  $K_4S_8$ , and 50 per cent. of the hydrosulphide was found unaltered* after solution of the sulphur had been effected. The following equations represent (i) the action expected, (ii) the change which actually took place.



The validity of the latter equation seems to be established, for the proportion KHS/S on the left hand side was that existing in the experiment  $\delta$  (see Table); and, of the three items on the right hand side, two were definitely established, the existence of  $K_4S_8$ , and the survival unaltered of 50 per cent. of the original hydrosulphide. It would follow then, from the fact that this proportion remains unaltered, that, by natural selection, under the given experimental conditions, the relation of the reacting materials is not that of the latter equation, but the simpler one:  $4KHS + S_6 = K_4S_8 + 2H_2S$ .

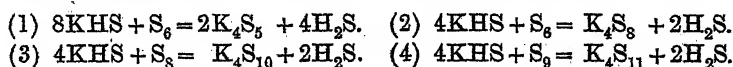
(6) As the result of treatment of crystals of  $K_4S_9$  and  $K_4S_8$ , with carbon disulphide, a lower polysulphide,  $K_4S_5 \cdot 10H_2O$ , has been obtained, which resists further removal of sulphur by this solvent.

Furthermore,  $K_4S_5$  is a stable polysulphide, mustard-yellow in colour, easily and completely soluble in water, and in it the following relation

exists,  $K_4S_2 \cdot S_8$ , that is, of the five sulphur atoms, three are in the polysulphide position. There seems, then, good reason for suggesting that the *prime product*, in the case of potassium polysulphides, is *tetrapotassium pentasulphide*,  $K_4S_5$ , and that the other crystalline polysulphides obtained are solid solutions of sulphur in this substance.

(7) Regard must also be paid to the fact that the polysulphides of ammonium and sodium are of the same degree of complexity, which seems to indicate that the source of this complexity is *in the sulphur molecule itself*. Now, it has long been held as a fact that sulphur, at temperatures above its boiling point, possesses a vapour density corresponding to a molecular formula of  $S_8$ , and that only as the temperature rises to  $860-1040^\circ$ , does it conform to the type  $S_2$ .\* During the past few years also, certain papers have appeared dealing with the molecular weight of sulphur in solution (compare Paternò and Nasini, *Ber.*, 1888, 21, 2153; Beckmann, *Zeit. physikal. Chem.*, 1890, 5, 76; Hertz, *ibid.*, 1890, 6, 358; Guglielmo, *Real. Accad. Linc.*, 1892, ii, 210; Orndorff and Terrasse, *Amer. Chem. J.*, 1895, 18, 173), and as a result of this work, the molecule of sulphur is stated to exist in solution as  $S_8$ ,  $S_8$ , or  $S_9$ .

Now the simplest expressions that can be written involving the action of such molecular groupings, and limited by the observed experimental behaviour of potassium hydrosulphide, are as follows :



Of these reactions, (2) and (3) have been already obtained, but for (1) and (4) the experimental conditions are not yet known.

A small portion of this work was carried out at the Royal Naval College, Greenwich, with the aid of Dr. W. J. McKerrow, and the remainder in the Davy-Faraday Research Laboratory of the Royal Institution. The author's thanks are given to the Managers of the Royal Institution for this privilege, and to Dr. A. Scott for kindly criticism and advice received during the course of the investigation.

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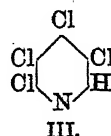
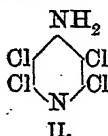
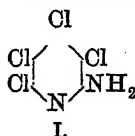
\* Biltz (*Ber.*, 1888, 21, 2153) does not, however, consider that the existence of gaseous molecules  $S_8$  can be established. He finds the vapour density varies *gradually* with the temperature.



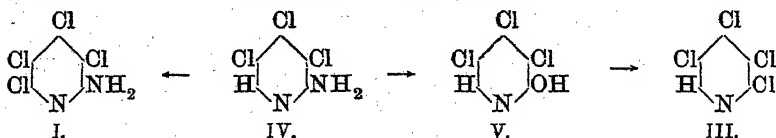
# LXVI.—Chlorine Derivatives of Pyridine. Part VI. Orientation of some Chloraminopyridines.

By W. J. SELL, M.A., F.R.S., and F. W. DOOTSON, M.A.

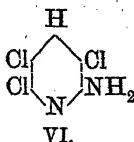
DURING the progress of the work an account of which has been given in this series of papers, a number of chloraminopyridines have been isolated and described, the structural formulæ of which are but very incompletely known. These compounds, so far as they have been examined, are remarkably stable, and although the fusing points in some cases do not widely differ yet such considerable variations are exhibited in their reactions that identification is rendered comparatively easy. The compounds dealt with are the trichloro- and tetrachloro-aminopyridines and as a basis recourse is had to three substances whose structural formulæ are known beyond doubt. These are (i) tetrachloro-2-aminopyridine (Trans., 1898, 73, 779; 1900, 77, 235), (ii) tetrachloro-4-aminopyridine (Amer. Chem. J., 1886, 6, 377; Trans., 1898, 73, 779; 1899, 75, 981), (iii) 3:4:5:6-tetrachloropyridine (Trans., 1900, 77, 2), and are thus represented :



In part III of this series of papers (Trans., 1899, 75, 980) a trichloraminopyridine was described which resulted from the interaction of sodium carbonate with a compound containing two pyridine nuclei. Since this trichloraminopyridine on treatment with phosphorus pentachloride yields a tetrachloraminopyridine identical with I, it follows that the amino-group in the original compound occupies relatively the 2-position and further that in the parent complex the nitrogen of one pyridine nucleus is united to the carbon atom in the 2-position, and not in the 3-position of the other as originally depicted (*loc. cit.*). It is here further shown that the hydrogen atom in this trichloraminopyridine occupies the 6-position by first converting the amino-group into a hydroxyl group in the usual manner and then heating the product at 182° in a sealed tube with phosphorus pentachloride. The result was a theoretical yield of 3:4:5:6-tetrachloropyridine. These changes may be represented thus :

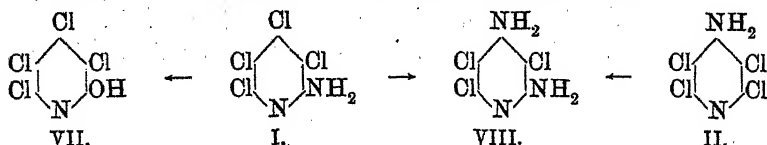


Similar work has been done in the case of the trichloraminopyridine derived from tetrachloroisonicotinic acid by heating the latter with ammonia (Trans., 1897, 71, 1083). From its genesis, the position of the hydrogen atom in this compound is beyond doubt, but with regard to that of the amino-group no experimental evidence was offered, it being merely suggested that from the known mobility of the chlorine atom occupying the position 2, the constitution of the substance was probably represented by the formula :



On heating a quantity of the trichloraminopyridine with phosphorus pentachloride, it was found that a theoretical yield of the tetrachloraminopyridine (m. p. 174—175°) represented by formula I was obtained, thus confirming the original conjecture with regard to it.

By the action of ammonia on pentachloropyridine (Trans., 1898, 73, 777) two tetrachloraminopyridines have been isolated one of which has been shown to have the constitution represented by formula II, the other, melting at 174—175°, is identical with I, a structure pointed out at the time as probable, but for which experimental evidence was wanting. From this compound a tetrachlorohydroxypyridine was obtained (*loc. cit.*) whose constitution VII is thus established. The two tetrachloraminopyridines mentioned above, on further treatment with ammonia and at a higher temperature, both yield the same trichlorodiaminopyridine (*loc. cit.*) which must therefore be represented by formula VIII. These derivatives are thus represented :



It may here be pointed out that the orientation of the compounds represented by formulæ IV and VI reduces the trichloraminopyridines whose constitutional formulæ are still unknown to two in number and in these cases the hydrogen atom must occupy either the 3- or the 5-position. One of these compounds, melting at 144—145°, is mentioned by Anschütz as resulting from the action of phosphorus pentachloride on  $\beta$ -hydroxyglutaramide (Richter's *Organische Chemie*, Ed. 1898, ii, 573 ; see also Trans., 1900, 77, 235).

## EXPERIMENTAL.

*Tetrachloro-2-aminopyridine from 3:4:5-Trichloro-2-aminopyridine.*

The trichloraminopyridine (m. p. 159—160°) derived from the compound containing two pyridine nuclei (Trans., 1899, '75, 980) by distillation with sodium carbonate solution, was heated for 4 hours in a sealed tube at 220—225° with a slight excess of phosphorus pentachloride, the cold mixture treated with water and distilled with steam, when a quantitative yield of the tetrachloraminopyridine melting at 174—175° (uncorr.) was obtained. On analysis:

0.1481 gave 14.9 c.c. nitrogen at 19° and 772 mm.  $N = 11.75$ .

0.1080 „ 0.267 AgCl.  $Cl = 61.30$ .

$C_5H_2N_2Cl_4$  requires  $N = 12.06$ ;  $Cl = 61.14$  per cent.

The properties of the compound thus obtained agree with those of tetrachloro-2-aminopyridine (Trans., 1900, '77, 236).

*Conversion of 3:4:5-Trichloro-2-aminopyridine into 3:4:5-Trichloro-2-hydroxyypyridine.*

Five grams of the compound were dissolved by the aid of a gentle heat in 80 c.c. of sulphuric acid containing approximately 80 per cent. of acid. After cooling, rather more than the theoretical quantity of potassium nitrite was added in small quantities at a time, the mixture heated on the water-bath for half an hour, with occasional agitation, and then, after cooling, poured into 500 c.c. of water. The new compound separated in flocks of fine needles, was filtered off, dissolved in dilute ammonia, to separate any traces of unaltered amino-compound, and again precipitated by the addition of hydrochloric acid.

The substance is readily soluble in alcohol, acetic acid, and most organic solvents. When recrystallised from boiling water, it separates on cooling, either in long, filamentous needles, or in flat needles which are quite colourless. On analysis:

0.527 gave 32 c.c. nitrogen at 15° and 752 mm.  $N = 7.04$ .

$C_5H_2OCl_3$  requires  $N = 7.05$  per cent.

When dissolved in warm, dilute ammonia, the ammonium salt, which is comparatively sparingly soluble in water, separates out on cooling in colourless, satiny, micaceous plates, which rapidly lose ammonia on exposure to air and become opaque. The potassium and sodium salts are much more soluble. The silver salt is thrown down as a jelly by precipitation from the ammonium salt.

*Conversion of 3:4:5-Trichloro-2-hydroxypyridine into 2:3:4:5-Tetrachloropyridine.*

Two grams of the hydroxy-compound were heated for an hour at  $182^{\circ}$  with 5 grams of phosphorus oxychloride and twice the theoretical amount of the pentachloride, the mixture treated with water and distilled in a current of steam. The product formed an oil which after the removal of the water solidified during the night. Examination showed that the compound, which melted sharply at  $21-22^{\circ}$ , was a pure specimen of 2:3:4:5-tetrachloropyridine. The yield was quantitative. It has been shown (Trans., 1898, 73, 440) that of the three tetrachloropyridines only that in which the chlorine atoms occupy the positions 2:3:4:5 will give a compound with mercuric chloride. On trying the experiment with a dilute alcoholic solution of this product, a semi-solid mass of the double salt was at once obtained, similar in every respect to the known compound.

*Conversion of 3:5:6-Trichloro-2-aminopyridine into Tetrachloro-2-aminopyridine.*

The trichloraminopyridine was mixed with phosphorus oxychloride and an excess of pentachloride and heated in a sealed tube for 4 hours at  $220-225^{\circ}$ . After decomposing the excess of the chlorides of phosphorus by water, the resulting mixture was distilled in a current of steam and the solid distillate purified by crystallisation from alcohol. The substance melted at  $174-175^{\circ}$  (uncorr.). The yield was quantitative. The following numbers were obtained on analysis:

0.1258 gave 12.7 c.c. nitrogen at  $16^{\circ}$  and 762 mm.  $N = 12.00$ .

0.1178 „ 0.2933 AgCl.  $Cl = 61.40$ .

$C_5H_2N_2Cl_4$  requires  $N = 12.06$ ;  $Cl = 61.14$  per cent.

The properties of the compound thus prepared agree in every respect with those of tetrachloro-2-aminopyridine (Trans., 1900, 77, 236).

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LXVII.—*Note on Partially Miscible Aqueous Inorganic Solutions.*

By G. S. NEWTH.

THE phenomena accompanying the partial miscibility of water with various organic liquids, and of organic liquids among themselves, have been studied by various observers and are quite familiar. With simple aqueous solutions of inorganic substances this is not the case, so that the following short note may be of interest.

When ordinary strong aqueous ammonia is shaken with a saturated solution of potassium carbonate and the mixture allowed to stand, two distinct liquids will be seen to separate out. Calling the two original liquids A and B, then one layer is a saturated solution of B in A while the other is a saturated solution of A in B. If A is the potassium carbonate solution, then at the ordinary temperature, after shaking together, solution A will have dissolved about 37 per cent. by volume of solution B, while solution B (the upper ammoniacal liquid) will contain about 6 per cent. of solution A.

The solubility of these two liquids in each other increases with rise of temperature, so that the composition of the two saturated layers or phases will gradually approximate until they are both identical, at which point the two liquids are miscible in all proportions.

Thus if we plot temperatures upon the vertical axis, and the percentage composition along the horizontal axis, the two curves representing the solubility of each liquid in the other will be seen to meet at a temperature of  $43^{\circ}$ , above which the two separate phases cease to exist and the liquids are miscible in all proportions.

For the experiments, the results of which are tabulated on these curves, A was a solution of potassium carbonate saturated (in contact with the solid) at the ordinary temperature. This solution was found to contain 57.2 grams of potassium carbonate in 100 c.c. Solution B was the so-called 0.880 ammonia. The sp. gr. of the sample actually used was 0.885 at  $16^{\circ}$ , corresponding to about 33 per cent. ammonia.

In order to determine the solubility of, say, solution B in A, a measured volume of the latter was first cooled to the required temperature. The potassium carbonate under these circumstances does not deposit crystals, but merely becomes supersaturated. Ammonia at the same temperature was added, and the mixture thoroughly shaken up in a tube closed by a cork; the ammonia being added until the mixture just began to show opalescence due to incipient separation of the two phases at the particular temperature.

At temperatures above  $30^{\circ}$ , the mixtures were confined in sealed tubes. The following figures were obtained:

Temp.	Solubility of A in B.		Solubility of B in A.	
	100 c.c. B dissolve A.	Mixture contains of solution A.	100 c.c. A dissolve B.	Mixture contains of solution A.
$1^{\circ}$	2.0 c.c.	2 per cent.	37.5 c.c.	72.7 per cent.
6	3.0	3	47.5	67.6
11	5.0	4.7	52.5	65.0
16	6.5	6.1	60.0	63.1
21	8.5	8.0	77.5	56.3
26	10.5	9.5	105.0	49.0
31	12.5	11.1	152.5	39.0
38	20.0	16.6	195	33.0
39	21.0	17	220	31.0
42	25.0	20	250	28.5
43	35.0	26	285	26.0

Not only is the mutual solubility of these two liquids promoted by rise of temperature, but it is greatly influenced by the addition of small quantities of water. The second pair of curves shows the solubility of A in B when to B has been added 10 per cent. of its volume of water, and the solubility of B in A when to the latter 10 per cent. of its volume of water has been introduced. These two curves are seen to meet at a temperature of  $25^{\circ}$ . At this point, the mixture contains 6.9 per cent. of added water, which has had the effect of lowering the temperature above which complete miscibility takes place (that is, the critical temperature of solution) from  $43^{\circ}$  to  $25^{\circ}$ .

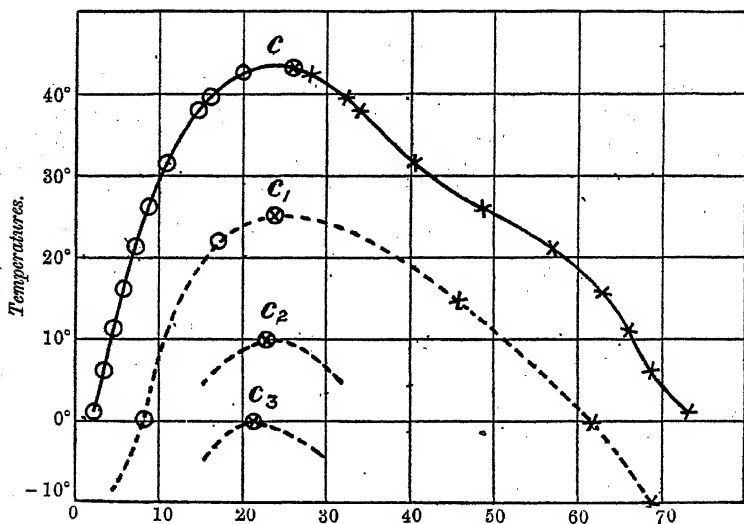
By the further addition of water, the point of intersection of the two solubility curves is still further lowered. Thus, when the added water amounts to 12.9 per cent. of the whole, the two phases cannot exist at temperatures above  $10^{\circ}$ ; whilst with 18.1 per cent. of added water the curves intersect at  $0^{\circ}$ , so that the liquids are now miscible in all proportions at all temperatures above the melting point of ice. These points are shown at  $C_1$ ,  $C_2$ , and  $C_3$  in the figure (p. 777).

It will be seen therefore that mixtures of solutions of potassium carbonate and ammonia can be produced which are critical for any desired temperature between certain pretty wide limits. Above the particular temperature, the solution remains clear; at the critical temperature, it becomes turbid owing to the separation of the mixture into the two phases.

In view of the considerable quantity of water originally present in the saturated potassium carbonate solution and in the ammonia, it seems surprising that the comparatively small addition of water should

produce so marked an effect; it therefore occurred to me to try to obtain a mixture which should contain *less* water than is present when saturated potassium carbonate solution and 0.880 ammonia are employed.

When anhydrous potassium carbonate is added to strong ammonia, the solid first becomes pasty and gradually dissolves, forming a heavy liquid layer beneath the ammonia; at the same time, ammonia gas is disengaged. The carbonate appears to dissolve in the water at the expense, as it were, of some of the ammonia, for if the materials are confined in a sealed tube so that the ammonia cannot escape, very little



*Percentages of potassium carbonate solution.*

Observations marked O indicate solubilities of solution A in solution B.

" X " " B " A.

A=Potassium carbonate solution (saturated at 15°).

B=Aqueous ammonia (sp. gr. 0.885).

of the salt is dissolved. The mixing of the anhydrous salt with the ammonia is attended by an absorption of heat, and as the bottom layer is able to take up its maximum amount of ammonia, still leaving the upper liquid saturated with the gas, two layers of liquid are thus obtained in which the total proportion of water present is rather *less* than when the two aqueous solutions are separately prepared. Complete miscibility of the two liquids so obtained does not take place until a temperature of 60° is reached.

A number of experiments have been made in the hope of finding other aqueous inorganic solutions which exhibited a similar behaviour,

but so far without success. Saturated and supersaturated solutions have been used, and in many cases where they were completely miscible at the ordinary temperature the mixtures have been cooled to  $-60^{\circ}$ , when in the majority of instances solidification set in.

When the obvious substitution of saturated sodium carbonate for the potassium salt is made, it is found that the addition of ammonia results in the precipitation of a crystalline salt, presumably one of the hydrated carbonates. It may be mentioned that strong aqueous solutions of trimethyl- and triethyl-amine behave with potassium carbonate precisely as ammonia does, and they also throw down the same precipitate from saturated sodium carbonate.

*Addendum.*—Since the above was communicated to the Society, it has been brought to my notice that the observation had previously been made by Mr. B. S. Proctor (*Chem. News*, 1864, 9, 25), that when strong aqueous ammonia is added to a strong solution of potassium carbonate, two liquid layers are obtained. The conditions determining the separation of these liquids, and their mutual solubility, were not ascertained, and, moreover, some of the observations recorded are not confirmed by my experiments. Thus Mr. Proctor found that the two liquids became miscible on standing 24 hours, and that a heavy, crystalline precipitate was deposited, which, he concluded, was potassium carbonate. I have kept the solutions in contact for *two years* without the slightest indication of mixing taking place, and under no conditions does any precipitation of solid occur. G. S. N.

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## LXVIII.—*Racemic and Optically Active Forms of Amarine.*

By H. LLOYD SNAPE, D.Sc., Ph.D.

AN isomeride of amarine which melted at  $198^{\circ}$  was described by Snape and Brooke (*Trans.*, 1899, 75, 208). The object of the present paper is to give an account of some further investigations of this base.

Attempts were made, in the first instance, to discover a method of preparation which would give a larger yield than those already described, and whereby the use of the poisonous ammonium cyanide might be avoided. These attempts, however, were unsuccessful. (1) It was thought that hydrobenzamide, if heated to a higher tempera-



ture than that at which it is converted into amarine, might yield isoamarine: but only lophine and a small quantity of a substance melting at  $227^{\circ}$  were obtained. This latter was no doubt cyaphenin (m. p.  $231^{\circ}$ ), since it appeared on analysis to have the composition of this substance and resembled it in being very sparingly soluble in alcohol as well as in other properties. Professor Japp subsequently informed me that he had observed the formation of cyaphenin in the preparation of lophine by heating hydrobenzamide.\* (2) The action of heat on an alcoholic solution of hydrobenzamide in sealed tubes at  $120^{\circ}$  and in presence of a small quantity of potassium cyanide also failed to furnish isoamarine. A basic substance was indeed obtained by extraction of the product with hydrochloric acid after some benzaldehyde and ammonia had been removed by steam; but this, when recrystallised from alcohol, melted at  $209-210^{\circ}$  (isoamarine melts at  $198^{\circ}$ ), and on analysis gave figures agreeing fairly well with those required for the formula  $C_{30}H_{28}O_2N_2$ . I further investigated (3) the action of ammonia and benzaldehyde in alcoholic solution in presence of potassium cyanide, and (4)† of ammonia on benzaldehyde and benzoin in alcoholic solution; but, although the conditions were varied as much as possible, no isoamarine was obtained.

At this stage, Prof. Japp kindly communicated to me a method, which he had discovered in conjunction with Mr. Moir, whereby isoamarine is prepared from amarine by heating the latter with sodium (Trans., 1900, 77, 637). This method was employed with entirely satisfactory results, and nearly all the isoamarine required for subsequent experiments was obtained by it. An attempt was made to modify the process by starting with hydrobenzamide, heating this for 4 hours at  $130^{\circ}$  to convert it into amarine, and then at once treating with sodium. It was thought that this would prove economical, hydrobenzamide as the source of amarine being the cheaper material; but, although the yield is good, the extra time and attention required are not repaid.

Having thus obtained an adequate supply of isoamarine, the attempts to determine wherein its constitution differs from that of ordinary amarine were continued.

*Action of Nitrous Acid.*—In the former paper, it was pointed out that only one hydrogen atom in the molecule of isoamarine could be

\* Japp and Moir have recently shown (Trans., 1900, 77, 640) that hydrobenzamide hydrochloride, when heated in hydrogen chloride, yields the corresponding salt of isoamarine.

† Radziszewski (*Ber.*, 1882, 15, 1495) states that amarine and many other products may be obtained by heating an alcoholic solution of benzoin and benzaldehyde with ammonia. This made it appear possible that isoamarine might be one of the products.

replaced by silver, thus indicating that probably only one imino-group was present. To ascertain whether this was the case, I endeavoured to prepare the nitroso-derivative or derivatives, but without success, although the methods of treating the hydrochloride of the base with alkali nitrite in aqueous solution, of allowing nitrous fumes to act on the base dissolved in chloroform, and of acting on the sulphate of the base with nitrosyl sulphate were all employed, and the two former methods were tried, both at the ordinary temperature and at 0°. A white crystalline substance was repeatedly obtained which gave the nitroso-reaction with phenol and sulphuric acid, but analyses showed that the nitroso-compound formed was probably mixed with nitrite and nitrate of the base. Its instability and the lack of a suitable solvent rendered its purification impossible.

*Action of Alkyl Iodides.*—Attempts to determine the presence of an imino-group were also made with ethyl iodide, but although isoamarine dissolves in boiling ethyl iodide and does not separate again on cooling, no pure compound could be isolated from the smeary mass which results on evaporation. An attempt to obtain an ethyl derivative by the action of isoamarine silver,  $C_{21}H_{17}N_2Ag$ , on ethyl iodide also failed. Methyl iodide reacts energetically with isoamarine silver, but again no pure product could be isolated. Further experiments on the action of alkyl iodides are being made.

*Action of Acetyl Chloride.*—Ordinary amarine and acetyl chloride are known to react in ethereal solution. In performing analogous experiments with isoamarine, ethyl acetate or chloroform was employed as the solvent, isoamarine being almost insoluble in ether. An unstable, white substance was obtained on removing, by evaporation, the excess of solvent and adding ether; but it decomposed at the ordinary temperature and could not be analysed in an unchanged condition. When alcohol was added to the reacting substances immediately after the removal of the excess of the solvent, and the liquid allowed to very slowly evaporate after standing for some time in a closed flask, some well-marked, six-sided plates which melted at 144—145°, were obtained, but only in very small quantity.

*Action of Nitric Acid.*—This was examined under various conditions: and reaction undoubtedly occurred in every instance, but in no case did a homogeneous nitro-derivative appear to be obtainable from the product. The products of nitration were apparently decomposed by water.

In short, whilst isoamarine appears to enter readily into many reactions, the products are generally, with the exception of such salts as were described in the former paper, so unstable as to present very great difficulty in isolating them in a sufficiently pure condition to determine their constitution. It would be interesting to examine whether

the optically active constituents of isoamarine, to be described later in this paper, lend themselves more readily to the formation of derivatives.

At this stage, as the result of a further communication from Prof. Japp, in which he kindly informed me that he had been led, as the result of his own experiments, to regard ordinary amarine as a *cis*-(meso-)diphenyl derivative and that isoamarine might be the *trans*-(racemoid)form, I determined to carry out an earlier intention of testing whether isoamarine was not merely a stereoisomeride of amarine. My experiments completely confirmed the theory which has been so fully and satisfactorily elaborated by Japp and Moir in their recent paper (*Trans.*, 1900, '77, 608); and have led to the resolution of isoamarine into its enantiomorphous constituents by means of tartaric acid.

#### SEPARATION OF ISOAMARINE INTO ITS OPTICALLY ACTIVE CONSTITUENTS.

In the first experiment, which resulted in the separation of acid tartrates of *d*- and *l*-isoamarine, 10 grams of isoamarine were added in successive portions to a solution of 5 grams of tartaric acid (that is, in the proportion theoretically required to form the acid tartrates) in 200 c.c.\* water heated nearly to its boiling point. The solution cooled without any separation having occurred, but this took place upon rubbing. The material thus separated was again dissolved by heating, and the whole left overnight. In this way, 6.5 grams were obtained of small, whitish-yellow, concretionary masses interspersed with some colourless needles. A second crop, weighing 4.65 grams, of prismatic crystals united to form plate-like or fan-shaped aggregates, was obtained on evaporating the filtrate by one-third. To induce crystallisation in this case, it was necessary to throw in some crystals which had been obtained by rubbing some of the liquid on a watch glass. A third crop, consisting of single needles and weighing 0.8 gram, was obtained by evaporating the filtrate from the second crop to one-half: a fourth crop was also prepared.

A saturated alcoholic solution of the first crop was found to be dextrorotatory; the second crop and also the final mother liquor were, on the other hand, levorotatory. This appeared to indicate that *d*-tartrates of *d*- and *l*-isoamarine had been formed and at least partially separated: there was no indication that any free tartaric acid had remained in the solution.

To confirm this conclusion, portions of the first and second crops were separately dissolved in water, and the base present in each was

\* It is sometimes desirable to use a much larger proportion of water. On some occasions, over two-thirds of the total materials separated, owing to colder weather having ensued, even when 250 c.c. of water had been employed.

precipitated by ammonia and crystallised from "methylated" spirit. Alcoholic solutions of the crystalline bases were then examined in a polarimeter, and were found to be respectively dextro- and lævorotatory. Ordinary isoamarine, when similarly examined, was found to be optically inactive.

The first crop (dextrorotatory) obtained as above by crystallisation from solution of isoamarine in tartaric acid was recrystallised from alcohol, and, after drying in the air, was analysed. This proved to be an acid tartrate containing 2 mols. of water of crystallisation.

1.0046 lost 0.0765  $\text{H}_2\text{O}$  at  $100^\circ$ .  $\text{H}_2\text{O}=7.61$ .

After drying at  $100^\circ$ :

0.1972 gave 0.4833  $\text{CO}_2$  and 0.0980  $\text{H}_2\text{O}$ .  $\text{C}=66.84$ ;  $\text{H}=5.53$ .

0.1815 ,, 10.6 c.c. moist nitrogen at  $16.2^\circ$  and 758.3 mm.  $\text{N}=6.79$ .

0.1814 ,, 10.4 c.c. ,, ,,  $14^\circ$  ,, 758.55 mm.  $\text{N}=6.74$ .

$\text{C}_{21}\text{H}_{18}\text{N}_2\cdot\text{C}_4\text{H}_6\text{O}_6\cdot 2\text{H}_2\text{O}$  requires  $\text{C}=66.96$ ;  $\text{H}=5.36$ ;  $\text{N}=6.25$ ;  
 $\text{H}_2\text{O}=7.44$  per cent.

The fourth crop (lævorotatory), selected as being probably the freest from admixture with tartrate of the *d*-base, was also submitted to analysis, and proved to have the same composition. This was not recrystallised.

1.0706, air dried, gave 0.0802  $\text{H}_2\text{O}$  at  $100^\circ$ .  $\text{H}_2\text{O}=7.49$ .

0.1803, dried at  $100^\circ$ , gave 10.4 c.c. moist nitrogen at  $18.9^\circ$  and 753 mm.  $\text{N}=6.57$ .

Nitrogen determinations were also made of the dextro- and lævorotatory basic substances obtained respectively from the first and second crops of the tartrates, in order to confirm the conclusion that these substances have the composition of ordinary isoamarine.

Base (dextrorotatory), prepared from the first crop, recrystallised from methylated spirit:

0.1817 gave 14.82 c.c. moist nitrogen at  $13^\circ$  and 766 mm.  $\text{N}=9.71$ .

Base (lævorotatory) prepared from second crop:

0.1810 gave 14.5 c.c. moist nitrogen at  $19^\circ$  and 777.5 mm.  $\text{N}=9.42$ .

$\text{C}_{21}\text{H}_{18}\text{N}_2$  requires  $\text{N}=9.40$  per cent.

Later observations showed that, even when more than one-half of the total weight of the base and tartaric acid employed separate in the first crop of crystals, there was no difficulty in isolating, by recrystallisation, pure tartrate of the *d*-base. But it is very desirable to so arrange the conditions that, if possible, the first crop of crystals shall be somewhat less than, or at most only slightly in excess of, one-half of the total weight of the original materials, because it is always

difficult, and sometimes impossible, to recover the pure tartrate of the *L*-base under these circumstances. In one case of the kind, the crystals, when obtained, had a different appearance from those of the *lævorotatory* tartrate, and the base precipitated by ammonia consisted solely of optically inactive *isoamarine*. The *lævorotatory* tartrate is, in fact, so easily altered in some way, that attempts to recrystallise it did not succeed.

After some preliminary experiments, it was decided to employ solubility, in the first instance, as a means of determining the purity of the tartrates. The *dextrorotatory* tartrate, being less soluble than the *lævo*-variety, might be regarded as pure when it yielded a product of unaltered solubility after recrystallisation.

The percentage of first crop material (*dextrorotatory*), which had been recrystallised from water, present in a saturated aqueous solution at 13°, was found to be 0.18, 0.23, and 0.27 in three different preparations. The same material recrystallised three times in succession from spirit (instead of once from water) had a solubility of 0.17. It thus appeared that a single recrystallisation of the first crop of crystals was sufficient, under ordinary circumstances, to obtain the material in a practically pure condition.

As regards the second and later crops (*lævorotatory*), it has been already stated that attempts to recrystallise them do not succeed. Hence this means of purifying these products is not available. It was thought that if, upon examination, successive crops proved to possess practically the same solubility, they might be taken to consist of the *lævorotatory* tartrate in sufficiently pure condition. This was found to be actually the case. Thus, in one preparation of the tartrates, the percentage of material found in a saturated aqueous solution at 13°, of the second crop, was 1.52; in the case of the third crop, it was 1.53. It was, however, remarked that when a large instead of a small excess of material was taken for the determination, there was a slight increase in the quantity of material dissolved. Thus the same second and third crops, which in slight excess gave the solubilities 1.52 and 1.53, gave the higher values 1.67 and 1.73 respectively when larger quantities were used. This may show that neither of the crops in question was entirely free from admixture. It will, however, be observed that the very considerable difference in solubility of the two tartrates shown by the figures given above favours the assumption that their separation by practical crystallisation is fairly complete.

*Determinations of the Rotatory Powers of the Tartrates.*

*Dextrotartrate.*—Three specimens were examined. They were dissolved in 90 per cent. alcohol at the atmospheric temperature (about 13°).

1. First crop material crystallised three times from alcohol .....  $[\alpha]_D + 94.44^\circ$  ( $c = 1.65$ ).
2. First crop material crystallised twice from water .....  $+ 94.37$  ( $c = 1.66$ ).
3. No. 2 recrystallised from alcohol.....  $+ 95.62$  ( $c = 1.56$ ).

For the subsequent preparation of the base, the tartrate was only once recrystallised from alcohol, optical examination showing that this was sufficiently pure.

*Lævotartrate.*—Specimens were examined under the same conditions as before both as regards temperature and the nature of the solvent, but at a concentration of from 3 to 4 per cent. This concentration, like that of about 1.6 in the case of the dextrotartrate, corresponds to about the maximum at the temperature of working. Solutions of maximum concentration were employed in order that the amount of rotation might be as large as possible, the instrument used not giving very accurate readings. The values obtained for the *d*- and *l*-tartrate respectively were thus not strictly comparable.

1. Second crop material .....  $[\alpha]_D - 71.94^\circ$  ( $c = 4.01$ ).
2. Third " " of the same preparation .....  $- 65.03$  ( $c = 3.71$ ).
3. Third crop material of another preparation .....  $- 71.69$  ( $c = 3.75$ ).

The figures show little more variation than might be expected considering the character of the polarimeter employed, and thus support the inference derived from the solubility determinations, that these materials are fairly pure.

It may be mentioned that a determination in which absolute was substituted for 90 per cent. alcohol, gave a lower result,  $[\alpha]_D = - 58.55^\circ$  ( $c = 3.85$ ).

*Action of Heat on d- and l-Tartrates.*

In obtaining, for analysis, anhydrous material from the *d*- and *l*-tartrates, it was noticed that, in the case of the latter, the water of crystallisation was all expelled after the substance had been in the steam oven for  $1\frac{1}{2}$  to 2 hours, whereas in the case of the former, the substance had to be replaced in the steam oven several times before constant weight was attained. It was also observed that if melting

point tubes containing *d*- and *l*-tartrates respectively are plunged in a bath at a temperature of  $110^{\circ}$ , the *l*-tartrate at once melts in its water of crystallisation, and there may even be some ebullition, but the *d*-tartrate gives off water gradually without fusion. If, instead of being at once exposed to a temperature of  $110^{\circ}$ , the tubes are gradually raised in temperature, the *l*-tartrate shows change much below  $100^{\circ}$ , which is not the case with the *d*-isomeride.

On the other hand, the anhydrous tartrates ultimately obtained by drying at  $100^{\circ}$ , behave, when heated, exactly in the same manner, softening at  $180^{\circ}$ , becoming converted into a viscous mass at  $186^{\circ}$ , and decomposing with evolution of gas at  $187^{\circ}$ . Yet these anhydrous salts are distinct substances, for when dissolved in 90 per cent. alcohol, the original *d*- and *l*-tartrates appear to be reproduced, the solutions being dextro- and lævo-rotatory respectively, and to the same extent as the original salts.

*Determination of the Rotatory Power of the Bases.*

Five grams of the *d*- or *l*-tartrate were dissolved in water at a gentle heat, enough water being taken to retain the whole, or nearly the whole, in solution when cold. From the cold solution, the base was precipitated with ammonia. The washed bases were crystallised from methylated spirit. In dissolving the bases, the temperature was not allowed to rise above  $60^{\circ}$ , lest racemisation should occur; but subsequent observations showed that this precaution was unnecessary.

In determining the rotatory power of the bases, the solvent first employed was 90 per cent. alcohol, and the following results were obtained:

<i>Dextro-base in alcohol</i> .....	$[\alpha]_D + 42.44^{\circ}$ ( $c=1.08$ ).
	$+ 46.61$ ( $c=1.43$ ).
	$+ 55.00$ ; but, after 3 hours, $+ 41.66^{\circ}$
	( $c=1.50$ ).
<i>Lævo-base in alcohol</i> .....	$[\alpha]_D - 67.11^{\circ}$ ; but, after several hours,
	$- 28.94^{\circ}$ ( $c=1.49$ ).
	$- 31.77^{\circ}$ . After several hours practi-
	cally unaltered ( $c=1.39$ ).

According to these experiments, the rotatory power of an alcoholic solution of the *d*-base is considerably higher than that of an alcoholic solution of the same concentration of the *l*-base, when the rotation has become constant, whereas if these substances are antipodes, it would be expected that their rotatory power would be the same. It was found, however, that if ethyl acetate, in which the bases are more soluble than in alcohol, is employed as the solvent, practically equal

values are obtained for the rotatory power of the two bases. The following are the results obtained in ethyl acetate solution:

Dextro-base....	$[\alpha]_D + 62.02^\circ$	after 4 hours practically unaltered. ( $c = 4.81$ ).
Lævo-       ,,	$[\alpha]_D - 50.03$	after 7 hours, constant at $-58.65^\circ$ . ( $c = 4.93$ ).
,,       ,,	$-48.33$	after $6\frac{1}{2}$ hours, constant at $-61.30$ . ( $c = 4.88$ ).

Thus the rotatory power of the two bases in this solvent is practically the same *when the rotation has become constant*. It will be noticed that, whereas the solution of the *d*-base exhibited its constant rotatory power as soon as prepared, the solution of the *l*-base at first exhibited a lower rotatory power. Isoamarine, when examined in alcoholic solution, proved to be optically inactive; hence, so far as the optical properties of these substances are concerned, it stands to the two bases in the relation of a racemoid compound or a *dl*-mixture to two antipodes. A comparison of these substances as regards solubility, melting point, and specific gravity supports the view that the parent base is a truly racemoid compound, and not merely an externally compensated mixture.

*Solubility of the Bases.*—A saturated solution of isoamarine at  $14^\circ$  in 90 per cent. alcohol was found to contain 1.24 per cent. of the base,\* whereas saturated solutions of the *d*- and *l*-bases contained 3.01 per cent. and 3.05 per cent. respectively.

*Melting Point.*—The melting point of isoamarine is  $198^\circ$ , that of the *d*-base was found to be  $175$ — $176^\circ$ , and that of the *l*-base recrystallised from alcohol  $174$ — $175^\circ$ . The *l*-base thus appears to be less pure than the *d*-isomeride, as was also indicated by the determinations of its rotatory power, and as was indeed to be expected from the circumstance that the parent lævotartrate could not be purified by recrystallisation.

*Specific Gravity.*—The averages of the specific gravity determinations were:—for isoamarine 1.16, and for each of the optically active bases 1.12.

It will be observed that the facts as regards the solubility, melting point, and density of isoamarine on the one hand and of the active bases on the other, agree with the relationships between these properties exhibited by other substances, namely, that racemic forms which

\* In Snape and Brooke's paper on isoamarine, a description of its behaviour towards solvents was inadvertently omitted. The base dissolves readily in hot ethyl acetate, benzene, alcohol, or chloroform, and crystallises from these solutions on cooling. In benzene, it is very slightly soluble in the cold, and in ether it is almost insoluble.



have a higher melting point than the derived active forms have also a higher density, but a lower solubility than these.

### *Crystalline Form.*

Crystals of ordinary isoamarine suitable for measurement were never obtained, whether from solution in alcohol or in ethyl acetate, but those that form slowly in an alcoholic solution are seen by the use of a lens to have the general form of prisms, never very long, and are pointed at each end. Crystals of the dextro-base, of measurable size, were obtained by the slow evaporation of an alcoholic solution, but better crystals were obtained when ethyl acetate was the solvent employed. In the case of the lævo-base, measurable crystals were only obtained by slow evaporation of a solution in ethyl acetate. The crystals of the *d*- and *l*-bases when examined under a lens, differ from those of isoamarine in that the prisms do not appear pointed at both ends, but only at one.

Crystals of the *d*- and *l*-bases, prepared as above, have been measured by Mr. W. J. Pope, and the following is his account of the results. I beg to express my indebtedness to him for the trouble he has taken in this matter:

"The crystals of *d*- and *l*-isoamarine are colourless, transparent, orthorhombic prisms of glassy lustre; they are sphenoidally hemihedral, crystals of *d*-isoamarine (Fig. 1) showing the form  $o, -k\{111\}$ , whilst those of the *l*-isomeride (Fig. 2) show the form  $o, +k\{111\}$ . The crystals of the two substances are thus enantiomorphously related.

"The dominant form is  $p\{110\}$ , and the pinacoid  $a\{100\}$  is only observed as a narrow replacement; the pyramid form  $o\{111\}$  is small, but well developed. The crystals are elongated in the direction of the *c*-axis.

"There is a good cleavage parallel to  $p\{110\}$  and a poor conchoidal cleavage parallel to the pinacoid  $c\{001\}$ . The optic axial plane is  $a(100)$  and the *c*-axis is the acute bisectrix. The optic axial angle is large and greater for blue than for red light. The double refraction is strong and negative in sign.

FIG. 1.

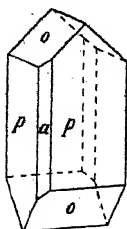
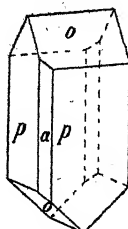


FIG. 2.



"Crystalline system. Orthorhombic: sphenoidal hemihedrism.

$$a : b : c = 1.4028 : 1 : 0.6750.$$

"Forms observed:—

"*d*-Isoamarine:  $a\{100\}$ ,  $p\{110\}$  and  $o$ ,  $-k\{111\}$ .

"*l*-Isoamarine:  $a\{100\}$ ,  $p\{110\}$ , and  $o$ ,  $+k\{111\}$ .

"The following angular measurements were made on crystals of both substances :

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$ap = 100 : 110$	28	$53^{\circ}16' - 55^{\circ}46'$	$54^{\circ}31'$	—
$pp = 110 : \bar{1}10$	16	$69^{\circ}42' - 72^{\circ}0'$	$70^{\circ}53'$	$70^{\circ}58'$
$ao = 100 : 111$	17	$67^{\circ}14' - 67^{\circ}59'$	$68^{\circ}7'$	$68^{\circ}15'$
$po = 110 : 111$	19	$49^{\circ}21' - 51^{\circ}8'$	$50^{\circ}16'$	$50^{\circ}20\frac{1}{2}'$
$oo = 111 : \bar{1}\bar{1}1$	17	$78^{\circ}10' - 80^{\circ}25'$	$79^{\circ}19'$	—
$oo = 111 : \bar{1}\bar{1}\bar{1}$	6	$116^{\circ}53' - 118^{\circ}4'$	$117^{\circ}31'$	$117^{\circ}23''$

*Synthesis of Isoamarine from the d- and l-Bases.*

When concentrated solutions of the *d*- and *l*-bases in 90 per cent. alcohol were mixed, a crystalline precipitate formed on rubbing. Under the microscope, the crystals could be seen to have the characteristic appearance of isoamarine and melted at  $197-198^{\circ}$ .

Solutions of *d*- and *l*-isoamarine in alcohol were respectively heated for many hours at  $100^{\circ}$ ,  $160^{\circ}$ , and  $200^{\circ}$ , but were not thereby racemised.

The result of the experiments detailed in this paper conclusively demonstrate that isoamarine is a racemoid isomeride of amarine and thus confirm the anticipations of Japp and Moir (*loc. cit.*).

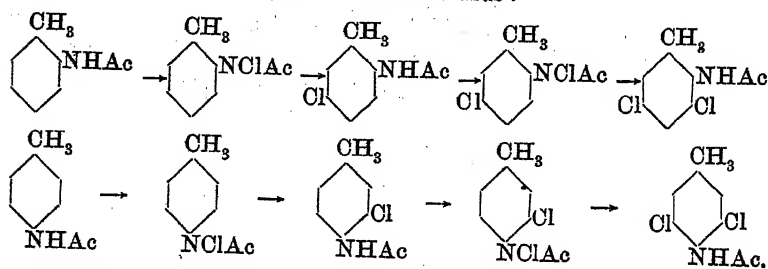
I have, in conclusion, to express my heartiest thanks to Dr. A. W. Day for the assiduous and able manner in which he has assisted me throughout this investigation.

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ABERYSTWYTH.

LXIX.—*Substituted Nitrogen Chlorides and Bromides derived from o- and p-Acetotoluidide.*

By F. D. CHATTAWAY and K. J. P. ORTON.

BOTH *o*- and *p*-acetotoluidide, when treated with hypochlorous or hypobromous acid, yield nitrogen chlorides and bromides which readily undergo transformation into the isomeric substituted toluidides; these in their turn form nitrogen chlorides and bromides which pass into the disubstituted toluidides, the aminic hydrogen of the latter being again replaceable by chlorine or bromine thus :



The bromine derivatives behave in a precisely similar manner. As with the substituted anilides, when the ortho- and para-positions to the acetylchloramino-group are occupied no further isomeric change takes place, hydrolysis or decomposition resulting from attempts to induce it.

The behaviour of the nitrogen chlorides and bromides derived from the toluidides is in entire agreement with the conclusion that substitution by chlorine or bromine in anilines and anilides is not a direct process, but a result of the transformation of a nitrogen chloride or bromide. The degree of ease or difficulty with which substitution in the toluidines and toluidides can be directly effected corresponds completely with the ease or difficulty with which the transformation of the corresponding nitrogen chloride or bromide can be brought about.

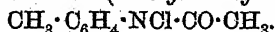
For example, *o*- and *p*-acetotoluidide can be converted into the monobromotoluidides with the greatest ease, and in agreement with this the corresponding nitrogen bromides are also transformed quantitatively.

On the other hand, the action of chlorine on *p*-acetotoluidide or bromine on 3-bromo-*p*-acetotoluidide yields tarry products, from which only with the greatest difficulty 3-chloro-*p*-acetotoluidide, or 3:5-dibromo-*p*-acetotoluidide, in small amount, can be isolated. Corresponding with this we find that the isomeric nitrogen chloride and bromide can only be transformed with great difficulty, a large part, under condi-

tions which affect the isomerisation, undergoing a more complicated change.

The properties of these nitrogen chlorides and bromides resemble exactly those of other members of the class (Trans., 1899, 75, 1046; 1900, 77, 134; *Ber.*, 1899, 32, 3573). The nitrogen chlorides are colourless, the nitrogen bromides sulphur-yellow solids all crystallising well in modifications of four-sided prisms, terminated by domes.

*o*-Acetylchloraminotoluene (*o*-Tolyl Acetyl Nitrogen Chloride),



Powdered *o*-acetotoluidide is shaken with excess of *N*/2 potassium hypochlorite containing potassium hydrogen carbonate. In a short time, a limpid, faintly yellow oil separates. This is dissolved in light petroleum (b. p. 50—80°), and from the solution the nitrogen chloride crystallises in star-shaped clusters of short, flattened prisms or plates melting at 43°.

0.1616 liberated *I* = 17.72 c.c. *N*/10 iodine. *Cl*, as *NCl*, = 19.44.

$\text{C}_9\text{H}_9\text{ONCl}$  requires *Cl*, as *NCl*, = 19.31 per cent.

This nitrogen chloride is extremely soluble in chloroform or benzene, and fairly soluble in light petroleum. On heating to 160°, sudden action occurs, the compound being mainly transformed into 5-chloro-*o*-acetotoluidide; the conversion, however, is accompanied by partial decomposition.

The isomeric change takes place slowly but quantitatively, when a solution of the nitrogen chloride in glacial acetic acid is kept at a temperature of 35—40°, about 36 hours being required for its completion. If a drop of concentrated sulphuric acid is added to the solution, the conversion is complete in a few minutes. A quick transformation is also brought about when the nitrogen chloride is placed in rapidly boiling water, but under these conditions 20—30 per cent. undergoes hydrolysis. A search was made for 3-chloro-*o*-acetotoluidide in the product of the transformation, but its presence could not be detected. *o*-Tolyl acetyl nitrogen chloride is comparatively stable, and can be kept for weeks in the absence of moisture without change.

*o*-Acetylchloramino-5-chlorotoluene (5-Chloro-*o*-tolyl Acetyl Nitrogen Chloride),  $\text{CH}_3 \cdot \text{ClC}_6\text{H}_3 \cdot \text{NCl} \cdot \text{CO} \cdot \text{CH}_3.$

This nitrogen chloride is easily prepared by agitating 5-chloro-*o*-acetotoluidide with a slight excess of *N*/2 bleaching powder solution just acidified with acetic acid. The compound is extremely soluble in chloroform or benzene, but only moderately soluble in acetic acid. It crystallises from light petroleum in short 4- or occasionally 6-sided prisms frequently terminated by domes, and melts at 66°.

0.2154 liberated I = 19.9 c.c. *N*/10 iodine. Cl, as :NCl, = 16.38.

$C_9H_9ONCl_2$  requires Cl, as :NCl, = 16.26 per cent.

When dissolved in glacial acetic acid, this nitrogen chloride undergoes transformation only very slowly at the ordinary temperature; but on boiling the solution for one hour it entirely changes into 3:5-dichloro-*o*-acetotoluidide (m. p. 185°).

Claus and Stapelberg (*Annalen*, 1893, 274, 291) prepared 3:5-dichloro-*o*-acetotoluidide by chlorinating *o*-acetotoluidide dissolved in alcohol and acetic acid. We find it far preferable to add gradually an excess of bleaching powder solution to one part of *o*-acetotoluidide dissolved in 5 parts of glacial acetic acid at the ordinary temperature, by which operation the nitrogen chloride of 5-chloro-*o*-acetotoluidide is formed. The latter is then separated, and heated with acetic acid until transformation is complete, when a nearly quantitative yield is obtained.

*o*-Acetylchloramino-3:5-dichlorotoluene (3:5-Dichloro-*o*-tolyl Acetyl Nitrogen Chloride),  $CH_3 \cdot C_6H_2Cl_2 \cdot NCl \cdot CO \cdot CH_3$ .

To prepare this compound, a solution of the 3:5-dichloro-*o*-acetotoluidide in acetic acid is treated with excess of *N*/2 bleaching powder solution at the ordinary temperature. The nitrogen chloride which separates as an oil is crystallised from light petroleum, in which it is very soluble. It forms short four-sided prisms, frequently with domed ends, and melts at 78°.

0.2037 liberated I = 16.1 c.c. *N*/10 iodine. Cl, as :NCl, = 14.01.

$C_9H_8ONCl_3$  requires Cl, as :NCl, = 14.04 per cent.

*p*-Acetylchloraminotoluene (*p*-Tolyl Acetyl Nitrogen Chloride),  $CH_3 \cdot C_6H_4 \cdot NCl \cdot CO \cdot CH_3$ .

This substance is prepared similarly to the corresponding ortho-derivative. To ensure complete conversion after treatment of the *p*-acetotoluidide with hypochlorous acid, it is best to dissolve the product in chloroform and to shake the liquid two or three times with a fresh solution of hypochlorous acid. It crystallises exceedingly well from light petroleum or from a mixture of this and chloroform in short, lustrous, four-sided prisms, which are often flattened or rhombic in appearance, and melts at 91–92°.

0.1524 liberated I = 16.5 c.c. *N*/10 iodine. Cl, as :NCl, = 19.20.

$C_9H_{10}ONCl$  requires Cl, as :NCl, = 19.31 per cent.

This nitrogen chloride when pure can be kept for months in a dry atmosphere and may even be heated to 175° without suffering any decomposition. If slightly impure or moist, it reddens on keeping,

and on heating decomposes rapidly even at  $100^{\circ}$  with development of colour and evolution of gas. Dissolved in chloroform, light petroleum, or acetic acid, it completely decomposes at the ordinary temperature in two or three days, and in an hour or so when warmed, with the formation of 3-chloro-*p*-acetotoluidide, *p*-acetotoluidide, and a red, oily substance. Heated in the presence of water, similar actions take place, and an amount of hydrochloric acid is liberated corresponding to about 14 per cent. of the nitrogen chloride used. When a few grams of the nitrogen chloride are decomposed by warming with acetic acid, to which two or three drops of sulphuric acid have been added, or by adding the powdered solid to boiling water, from 50—60 per cent. is transformed into 3-chloro-*p*-acetotoluidide. With larger quantities, however, the yield is much less and the chlorotoluidide difficult to purify. The behaviour of this nitrogen chloride accounts for the difficulties experienced by Lellmann and Klotz (*Annalen*, 1885, 231, 311) in preparing 3-chloro-*p*-acetotoluidide by direct chlorination of *p*-acetotoluidide dissolved in acetic acid. They were only able to obtain a 20 per cent. yield, and did not succeed in discovering the cause of this unsatisfactory result. We have reason to believe that a secondary reaction takes place, in which the methyl group interacts with the chlorine attached to the nitrogen.

*Preparation of 3-Chloro-p-toluidine.*—The following method gives a 50 per cent. yield of 3-chloro-*p*-toluidine from *p*-acetotoluidide.

Fifty grams of *p*-acetotoluidide are dissolved in 200 c.c. of glacial acetic acid and a small excess of *N*/2 bleaching powder solution added. Heat is evolved and a reddish oil separates, which solidifies on cooling. The dark red mass, which largely consists of 3-chloro-*p*-toluidide and *p*-acetotoluidide is boiled with alcohol and sulphuric acid. The acid is then partially neutralised and the still acid product distilled in steam. 3-Chloro-*p*-toluidine comes over first, and, after completely neutralising the acid, is followed by *p*-toluidine, which represents about 15 per cent. of the original *p*-acetotoluidide. A dark, oily substance remains in the distilling flask.

*p*-Acetylchloramino-3-chlorotoluene (3-Chloro-*p*-tolyl Acetyl Nitrogen Chloride),  $\text{CH}_3 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NCl} \cdot \text{CO} \cdot \text{CH}_3$ .

3-Chloro-*p*-acetotoluidide is dissolved in acetic acid and a slight excess of *N*/2 bleaching powder solution added. The oil which forms is separated, shaken with sodium hydrogen carbonate to remove acetic acid, and then recrystallised from light petroleum. It forms very short, flattened prisms, which frequently appear as diamond-shaped plates, and melts at  $48^{\circ}$ .

0.3167 liberated I = 29.3 c.c. *N*/10 iodine. Cl, as :NCl, = 16.35.

$\text{C}_8\text{H}_7\text{ONCl}_2$  requires Cl, as :NCl, = 16.26 per cent.

This nitrogen chloride, dissolved in glacial acetic acid, is transformed very slowly at the ordinary temperature into 3:5-dichloro-*p*-acetotoluidide. On boiling such a solution, a brilliant red colour develops and no nitrogen chloride remains after some fifteen minutes; on cooling, long needles of the dichlorotoluidide separate, but the yield does not amount to more than 50 per cent. of the theoretical.

*p*-Acetylchloramino-3:5-dichlorotoluene (3:5-Dichloro-*p*-tolyl Acetyl Nitrogen Chloride),  $\text{CH}_3 \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{NCl} \cdot \text{CO} \cdot \text{CH}_3$ .

This substance is prepared from the corresponding dichlorotoluidide exactly as the last, and is recrystallised from light petroleum. It forms thin, four-sided prisms, often 4—5 centimetres long, and melts at 72°.

0.1228 liberated I = 9.6 c.c. *N*/10 iodine. Cl, as :NCl, = 13.86.

$\text{C}_9\text{H}_8\text{ONCl}_2$  requires Cl, as :NCl, = 14.04 per cent.

*o*-Acetylbromaminotoluene (*o*-Tolyl Acetyl Nitrogen Bromide),  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NBr} \cdot \text{CO} \cdot \text{CH}_3$ .

This compound is obtained by treating finely divided *o*-acetotoluidide suspended in a dilute solution of potassium hydrogen carbonate with a slight excess of a solution of hypobromous acid, keeping the temperature below 0°. Action takes place rapidly, the toluidide losing its crystalline form and becoming pale yellow in colour. The nitrogen bromide can be crystallised from a mixture of chloroform and light petroleum, from which it separates as pale yellow, four-sided plates melting at 100.5°. It is readily soluble in chloroform or benzene, but only slightly so in light petroleum.

0.2530 liberated I = 22.25 *N*/10 iodine. Br, as :NBr, = 35.16.

$\text{C}_9\text{H}_{10}\text{ONBr}$  requires Br, as :NBr, = 35.07 per cent.

This nitrogen bromide, on rapidly heating, melts sharply at 100.5°, but on keeping about 10 seconds at this temperature transformation takes place, accompanied by evolution of heat, and the whole solidifies to a slightly brown, crystalline mass of 5-bromo-*o*-acetotoluidide, which melts only a few degrees below 160°.\* This transformation takes place very readily if the compound is heated under water, or still better if it is dissolved in glacial acetic acid and the solution allowed to stand at the ordinary temperature for 24 hours. The transformation appears to be quantitative; we have never observed the formation of any other product.

\* 5-Bromo-*o*-acetotoluidide, when pure, melts sharply at 160°, not at 156—15, as usually given.

*o*-Acetylbromamino-5-bromotoluene (5-Bromo-*o*-tolyl Acetyl Nitrogen Bromide),  $\text{CH}_3 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NBr} \cdot \text{CO} \cdot \text{CH}_3$ .

This nitrogen bromide was prepared exactly as above, but to ensure complete conversion, the product, which clots together, was dissolved in chloroform and the solution thoroughly shaken with more hypobromous acid containing potassium hydrogen carbonate. The solid, obtained by evaporating off the chloroform, was recrystallised from chloroform and light petroleum. The crystals are brilliant yellow, apparently rectangular, plates melting at  $91^\circ$ .

0.3852 liberated  $\text{I} = 25.1$  c.c. *N*/10 iodine. Br, as  $\cdot\text{NBr}$ , = 26.05.

$\text{C}_9\text{H}_5\text{ONBr}_2$  requires Br, as  $\cdot\text{NBr}$ , = 26.05 per cent.

When 2-methyl-4-bromophenyl acetyl nitrogen bromide is heated above its melting point at about  $110$ — $120^\circ$ , it darkens somewhat in colour and is transformed into the isomeric 3:5-dibromo-*o*-acetotoluidide, this then slowly solidifies to a light brown, crystalline mass, which melts not very sharply at about  $170^\circ$ . A certain amount of decomposition always accompanies the transformation, this being more marked the more rapid the heating.

This isomeric change takes place readily when the nitrogen bromide is heated with water at  $100^\circ$ , although here a certain amount of hydrolysis accompanies it, or when the compound is heated at  $100^\circ$  with glacial acetic acid in a sealed tube. On recrystallising the product, 3:5-dibromo-*o*-acetotoluidide is obtained in long, colourless needles which melt at  $205^\circ$ .

*o*-Acetylbromamino-3:5-dibromotoluene (3:5-Dibromo-*o*-tolyl Acetyl Nitrogen Bromide),  $\text{CH}_3 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{NBr} \cdot \text{CO} \cdot \text{CH}_3$ .

3:5-Dibromo-*o*-acetotoluidide is also readily converted as above by hypobromous acid into its nitrogen bromide, which crystallises well from petroleum (b. p.  $80$ — $100^\circ$ ) in characteristic brilliant yellow, four-sided plates melting at  $120^\circ$ .

0.4526 liberated  $\text{I} = 23.25$  c.c. *N*/10 iodine. Br, as  $\cdot\text{NBr}$ , = 20.54.

$\text{C}_9\text{H}_4\text{ONBr}_3$  requires Br, as  $\cdot\text{NBr}$ , = 20.72 per cent.

*p*-Acetylbromaminotoluene (*p*-Tolyl Acetyl Nitrogen Bromide),  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NBr} \cdot \text{CO} \cdot \text{CH}_3$ .

*p*-Acetotoluidide in a finely divided state was suspended in a very dilute solution of potassium hydrogen carbonate containing ice, about half times the theoretical quantity of a solution of hypobromous acid below  $0^\circ$  added quickly, and the whole stirred for a few



minutes. The pale yellow product was then crystallised from a mixture of chloroform and light petroleum.

*p*-Tolyl acetyl nitrogen bromide forms brilliant yellow, four-sided prisms terminated by domes, one side of the latter being very largely developed. It is extremely unstable; exposed to the moist air of a laboratory, it becomes in a few minutes of a pale pink colour, which deepens on standing to a full red, whilst the melting point continuously falls. The crystals can, however, be kept in an exhausted desiccator for several hours without change.

0.3059 liberated I = 26.9 c.c. *N*/10 iodine. Br, as :NBr, = 35.15.

$C_9H_{10}ONBr$  requires Br, as :NBr, = 35.07 per cent.

On heating quickly it melts at 94–95° to a pale yellow liquid, but at this temperature rapid transformation into 3-bromo-*p*-acetotoluidide goes on, and in a few seconds the melted mass crystallises. Transformation also takes place quickly at a lower temperature; when heated at 50° for a few minutes the crystals slowly liquefy and resolidify to a pale pink, crystalline mass, which again melts only 2–3° below the melting point of the *p*-bromotoluidide. This isomeric change goes on slowly at the ordinary temperature, and even to a considerable extent below 0°. When the nitrogen bromide is warmed with water, or dissolved in chloroform or glacial acid, and the solution allowed to stand for a few hours, complete transformation takes place and the change is practically quantitative, although a pale pink colour is developed. Pure 3-bromo-*p*-acetotoluidide can be obtained in long, white prisms by once crystallising the transformation product from alcohol. The behaviour of this nitrogen bromide offers a marked contrast to that of the corresponding nitrogen chloride.

*p*-Acetyl bromamino-3-bromotoluene (3-Bromo-*p*-tolyl Acetyl Nitrogen Bromide),  $CH_3 \cdot C_6H_3Br \cdot NBr \cdot CO \cdot CH_3$ .

This was prepared in the ordinary way by the action of hypobromous acid on 3-bromo-*p*-acetotoluidide, and was crystallised from a mixture of chloroform and light petroleum. It forms pale yellow, four-sided plates which melt at 87°.

0.2745 liberated I = 17.9 c.c. *N*/10 iodine. Br, as :NBr, = 26.07.

$C_9H_9ONBr_2$  requires Br, as :NBr, = 26.05 per cent.

On heating above its melting point, it decomposes between 100° and 110°, yielding a red, tarry product which does not crystallise. A similar viscous substance is formed when the nitrogen bromide is heated at 100° in a sealed tube with a little glacial acetic acid. The product is soluble in alcohol or acetic acid, but a thick yellow oil is deposited

on cooling. If this is removed from time to time and the solution boiled with animal charcoal, 3:5-dibromo-*p*-acetotoluidide (m. p. 206°) finally crystallises out; the yield of the latter, however, is only about 10 per cent. of the theoretical. In this action, the normal transformation of the nitrogen bromide into the isomeric bromotoluidide is complicated by another action in which the methyl group is probably attacked by the bromine attached to the nitrogen.

The extent to which the latter action takes place when the nitrogen chlorides and bromides derived from the toluidides undergo the normal isomeric change apparently depends on the relative difficulty with which transformation takes place. When isomeric change occurs readily and at a low temperature as with *o*- and *p*-tolyl acetyl nitrogen bromides, this is practically the sole action; when, however, it cannot be easily effected, and only at a relatively high temperature, it is accompanied by the other reaction.

*p*-Acetylbromamino-3:5-dibromotoluene (3:5-Dibromo-*p*-tolyl Acetyl Nitrogen Bromide),  $\text{CH}_3\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{NBr}\cdot\text{CO}\cdot\text{CH}_3$ .

3:5-Dibromo-*p*-acetotoluidide (m. p. 206°) also easily yields a nitrogen bromide on treatment with hypobromous acid. To ensure complete conversion, it is best to dissolve the product in chloroform, and then to stir or shake this for an hour or so with excess of a fresh solution of hydrobromous acid containing a little potassium hydrogen carbonate. On evaporating off the chloroform or adding light petroleum, the nitrogen bromide separates in brilliant, yellow, short, four-sided prisms terminated by domes and melts at 118°.

0.3929 liberated I = 20.2 c.c. *N*/10 iodine. Br, as :NBr, = 20.55.

$\text{C}_9\text{H}_8\text{ONBr}_3$  requires Br, as :NBr, = 20.72 per cent.

#### *Method of Transforming Nitrogen Chlorides and Bromides.*

The transformation of nitrogen chlorides and bromides is generally best effected by allowing a solution in a little glacial acetic acid to stand at the ordinary temperature, or, when necessary, heating it in a sealed tube. Acetic anhydride may occasionally be employed as solvent when the substances are hydrolysed exceptionally readily, as is the case with some nitrogen bromides. Addition of a drop of sulphuric acid is in some cases advantageous, as in the transformation of the nitrogen chloride of *p*-acetotoluidide. With the more readily transformable compounds, heating under water is sufficient, although this generally causes some hydrolysis.

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LXX.—*Ortho-substituted Nitrogen Chlorides and Bromides and the Entrance of Halogen into the Ortho-position in the Transformation of Nitrogen Chlorides.*

By F. D. CHATTAWAY and K. J. P. ORTON.

IN our earlier papers (Trans., 1899, 75, 1046; Ber., 1899, 32, 3573) on substituted nitrogen chlorides and bromides, it was stated that we had so far not observed the simultaneous formation of ortho- and para-derivatives in their isomerisation. The transformation products of phenyl acetyl nitrogen chloride and phenyl acetyl nitrogen bromide, for example, melted within a degree or so of the isomeric *p*-chloro- and *p*-bromo-acetanilides, and could be obtained perfectly pure by one crystallisation from alcohol.

In order, however, to decide this point definitely, we have prepared larger quantities of phenyl acetyl nitrogen chloride, phenyl acetyl nitrogen bromide, and phenyl benzoyl nitrogen bromide, and have made a careful search, in the products of their transformation, for small amounts of *o*-chloroacetanilide, *o*-bromoacetanilide and *o*-bromobenzanilide respectively.

When phenyl acetyl nitrogen chloride is transformed, we find that *o*-chloroacetanilide is produced together with *p*-chloroacetanilide. The transformation product consists of about 95–96 per cent. of the para- and 4–5 per cent. of the ortho-compound.

We have failed to isolate any *o*-bromoacetanilide or *o*-bromobenzanilide from the transformation products of the isomeric nitrogen bromides, and although from analogy these probably are formed, the amount produced must be exceedingly small, certainly less than one per cent. under the conditions of transformation which we have studied.

When these nitrogen bromides are worked with on a large scale, the problem is complicated by a certain amount of hydrolysis occurring, and by the consequent reformation of a small amount of unsubstituted anilide.

The behaviour of these nitrogen halogen compounds is in marked contrast with that of the nitramines (Bamberger, Ber., 1897, 30, 1248), which, when this is possible, always undergo transformation into both ortho- and para-derivatives, the former often being the chief, if not the only, product.

We have also prepared *o*-chlorophenyl acetyl nitrogen chloride and *o*-bromophenyl acetyl nitrogen bromide by the action of hypochlorous

and hypobromous acid respectively on the corresponding substituted anilides.

The physical and general chemical properties of these compounds are typical of the nitrogen chlorides and nitrogen bromides, but they are relatively more stable and may be heated moderately or kept for a long time without alteration. Isomeric change can, however, be effected readily, and they then undergo transformation into the 2:4-disubstituted acetanilides.

*Transformation of Acetylchloraminobenzene (Phenyl Acetyl Nitrogen Chloride).*

One hundred grams of acetanilide were converted into the nitrogen chloride by the method already described (Trans., 1899, 75, 1046). The pure chloride was placed under water, acidified with acetic acid, and ice added to prevent the temperature rising. In an hour transformation was complete; the product was then hydrolysed by boiling for six hours with alcohol and sulphuric acid. On cooling, the larger part of the *p*-chloroaniline separated out as sulphate. This was filtered off and the alcohol evaporated from the mother liquor, which was then subjected to steam distillation after partially neutralising the acid. A liquid base came over in small quantity. This was acetylated and the crude anilide, which melted at 72°, was recrystallised from benzene and light petroleum (b. p. 50—80°) until it melted constantly at 87°, the melting point of *o*-chloroacetanilide. A yield of between 4 and 5 per cent. of the theoretical amount was obtained. As a confirmation, the percentage of chlorine was determined.

0.1411 yielded 0.1204 AgCl. Cl = 21.1.

$C_6H_4Cl \cdot NH \cdot CO \cdot CH_3$  requires Cl = 20.9 per cent.

A similar method of procedure was adopted in studying the transformation products of phenyl acetyl nitrogen bromide and phenyl benzoyl nitrogen bromide. Five hundred grams of the former were transformed by rapidly heating with water, and 60 grams of the latter by allowing it to stand for a few hours in a moist state at the ordinary temperature. After treating the transformed products as above, the small quantity of material distilling over after partial neutralisation was in each case shown to be a mixture of *p*-bromoaniline and aniline by acetylating and benzoylating respectively, finding the percentage of bromine in the recrystallised product, and comparing its melting point with that of a similar mixture crystallised from a prepared solution containing anilide and *p*-bromoanilide. The product obtained from the transformed material melted within a degree or so of the melting point of the known mixture.

*Acetylchloramino-2-chlorobenzene (o-Chlorophenyl Acetyl Nitrogen Chloride),  $C_6H_4Cl \cdot NCl \cdot CO \cdot CH_3$ .*

*o*-Chloroacetanilide is treated with an excess of a solution of potassium hypochlorite containing potassium hydrogen carbonate. After about 1 hour the conversion into the nitrogen chloride is complete. The latter is very soluble in chloroform, benzene, or acetic acid, but only moderately so in hot petroleum (b. p. 50—80°). It forms long, flattened, exceedingly lustrous prisms which melt at 88°.

0.2901 liberated  $I = 28.8$  c.c. *N*/10 iodine.  $Cl$ , as  $:NCl$ , = 17.59.

$C_6H_4Cl \cdot NCl \cdot CO \cdot CH_3$  requires  $Cl$ , as  $:NCl$ , = 17.38 per cent.

On heating the molten substance, no sudden transformation takes place, but decomposition with darkening occurs about 170°.

This nitrogen chloride is unusually stable and can be recrystallised from glacial acetic acid; even heating its solution in glacial acetic acid for several hours at 100° does not complete the isomeric change, a mode of treatment which would have caused the immediate transformation of any other nitrogen chloride with the para-position unoccupied. On heating under boiling water, it partially hydrolyses and partially transforms into 2:4-dichloroacetanilide. Heated in a sealed tube at 140° in the presence of a little acetic acid, 2:4-dichloroacetanilide is rapidly formed. No 2:6-dichloroacetanilide has been recognised in the product of transformation.

*Acetylbromamino-2-bromobenzene (o-Bromophenyl Acetyl Nitrogen Bromide),  $C_6H_4Br \cdot NBr \cdot CO \cdot CH_3$ .*

*o*-Bromoacetanilide in a finely powdered state was suspended in a dilute solution of potassium hydrogen carbonate containing an excess of hypobromous acid, and the whole stirred for several hours. The nitrogen bromide was then recrystallised from chloroform and light petroleum. It separates in pale yellow, four-sided prisms with domed ends, and melts at 150—152° with slight decomposition. Heated above this temperature, the yellow liquid darkens in colour and at 160° decomposes suddenly, bromine being evolved and a dark brown mass left.

0.1968 liberated  $I = 13.4$  c.c. *N*/10 iodine.  $Br$ , as  $:NBr$ , = 27.22.

$C_6H_4Br \cdot NBr \cdot CO \cdot CH_3$  requires  $Br$ , as  $:NBr$ , = 27.29 per cent.

On heating for some hours at 100° with a little water, it is partially hydrolysed and partially transformed into 2:4-dibromoacetanilide melting at 146°. This latter transformation alone takes place when the nitrogen bromide is heated in a sealed tube with a

few drops of glacial acetic acid at  $140^{\circ}$  for about an hour. *o*-Chloroformanilide and -benzanilide and *o*-bromoformanilide and -benzanilide also yield nitrogen chlorides and nitrogen bromides.

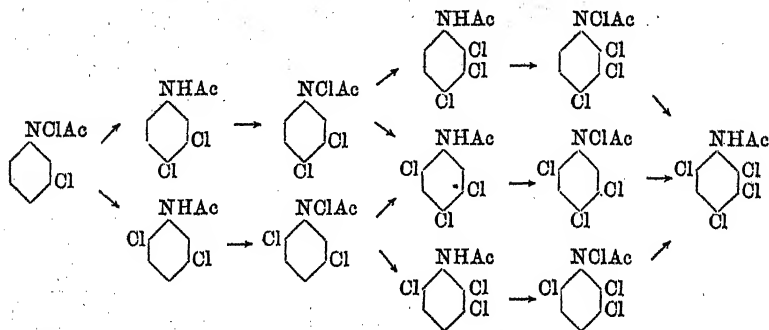
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### LXXI.—*Nitrogen Chlorides derivable from m-Chloroacetanilide and their Transformation.*

By F. D. CHATAWAY, K. J. P. ORTON, and W. H. HURTLEY.

THE study of the behaviour of hypochlorous acid with *m*-chloroacetanilide has led to results similar to those observed in the case of acetanilide and the acetotoluidides (Trans., 1899, 75, 1046; 1900, 77, 134). *m*-Chloroacetanilide yields a nitrogen chloride, which undergoes transformation into 3:4- and 2:5-dichloroanilide. Each of these again readily forms a nitrogen chloride. That from the 3:4-derivative, on isomerisation, gives a mixture of the 2:3:4- and 2:4:5-trichloroacetanilide, whilst the nitrogen chloride of the 2:5-isomeride yields the 2:4:5- together with the hitherto unknown 2:3:6-trichloroacetanilide. Finally, the 2:3:4-, 2:4:5-, and 2:3:6-trichloro-derivatives yield nitrogen chlorides, all of which undergo transformation into 2:3:4:6-tetrachloroacetanilide. A mixture of these three nitrogen chlorides is obtained when a solution of *m*-chloroacetanilide in acetic acid is heated with excess of bleaching powder.

The following scheme represents the transformations:



With these nitrogen chlorides, the formation of ortho-derivatives takes place to a much greater extent than in the transformation of phenyl acetyl nitrogen chloride. In the latter case, only about 5 per cent. of *o*-chloroacetanilide is obtained, whilst more than 20 per cent.

of 2:5-dichloroacetanilide is produced from *m*-chlorophenyl acetyl nitrogen chloride. In no instance, however, does the quantity of the ortho-derivative exceed or even approach that of the para-isomeride.

The nitrogen chlorides of this series have all the general characters of the group. Their crystalline form is of the usual four-sided prism type, but the prisms are frequently very slender and aggregated in clusters. They are all stable and difficult to isomerise. Although all the positions in *m*-chlorophenyl acetyl nitrogen chloride into which the chlorine atom may wander are vacant, transformation is only complete after several days, when the compound, dissolved in acetic acid, is allowed to stand at the ordinary temperature. Under similar conditions, phenyl acetyl nitrogen chloride undergoes transformation in a few minutes, and *p*-chlorophenyl acetyl nitrogen chloride in a few hours. The 3:4-dichlorophenyl acetyl nitrogen chloride, in which both ortho-positions are unoccupied, is not completely transformed after the solution in acetic acid has stood for six weeks. The isomeric change of the nitrogen chlorides of the three trichloroacetanilides can only be effected at a high temperature (160—180°), and is always accompanied by much hydrolysis.

*Acetylchloramino-m-chlorobenzene (m-Chlorophenyl Acetyl Nitrogen Chloride),*  $C_6H_4Cl \cdot NCl \cdot CO \cdot CH_3$ .

*m*-Chloroacetanilide is rapidly converted into this nitrogen chloride when treated with a *N*/2 solution of hypochlorous acid in presence of potassium hydrogen carbonate. The compound is purified by recrystallising from light petroleum (b. p. 50—80°), from which it separates in star-shaped clusters of very small prisms melting at 93°.

0.3532 liberated  $I = 17.44$  c.c. *N*/10 iodine.  $Cl$ , as  $:NCl$ , = 17.51.

0.1988 gave 0.2782  $AgCl$ . Total,  $Cl = 34.61$ .

$C_6H_4Cl \cdot NCl \cdot CO \cdot CH_3$  requires  $Cl = 34.76$  per cent;  $Cl$ , as  $:NCl$ , = 17.38.

When heated under water or in solution in acetic acid, hydrolysis, and not isomeric change, takes place. Molecular transformation is best brought about by allowing a cold solution in acetic acid to stand for 7 to 10 days. The products are 3:4- and 2:5-dichloroacetanilide, the former of which largely predominates. Separation is effected by hydrolysing the anilides and distilling the aniline sulphates in steam in presence of sulphuric acid. 2:5-Dichloroaniline comes over, and, on cooling, the very sparingly soluble sulphate\* of the 3:4-compound separates from the mother liquor in pearly leaves.

\* 1.2405 gave 0.7063  $BaSO_4$ .  $SO_4 = 23.43$ .

$(C_6H_3Cl_2 \cdot NH_2)_2 \cdot H_2SO_4$  requires  $SO_4 = 22.78$  per cent.

The 3:4-dichloroaniline obtained from this was purified by distilling under diminished pressure; its boiling point was 145° at 15 mm.

*Acetylchloramino-3:4-dichlorobenzene (3:4-Dichlorophenyl Acetyl Nitrogen Chloride),  $C_6H_3Cl_2 \cdot NCl \cdot CO \cdot CH_3$ .*

This compound is best prepared by adding 3:4-dichloroacetanilide to  $N/2$  bleaching powder solution just acidified with acetic acid. It crystallises from light petroleum in clusters of small, needle-like prisms melting at  $92^\circ$ .

0.2443 liberated  $I = 10.35$  c.c.  $N/10$  iodine.  $Cl$ , as  $:NCl$ , = 15.02.

$C_6H_3Cl_2 \cdot NCl \cdot CO \cdot CH_3$  requires  $Cl$ , as  $:NCl$ , = 14.87 per cent.

Dissolved in acetic acid, it undergoes transformation very slowly, and the change is not complete after six weeks. The major portion of the nitrogen chloride has changed, however, after ten days into two trichloroanilides, which can be separated by fractional crystallisation from 50 per cent. acetic acid, in which 2:4:5-trichloroacetanilide melting at  $190^\circ$  (Beilstein and Kurbatoff, *Annalen*, 1879, 196, 214, give  $184-185^\circ$ ) is very sparingly soluble. From the mother liquor, 2:3:4-trichloroacetanilide\* separates in fine needles melting at  $123^\circ$ . The latter compound forms about 25 per cent. of the mixed anilides.

*Acetylchloramino-2:5-dichlorobenzene (2:5-Dichlorophenyl Acetyl Nitrogen Chloride),  $C_6H_3Cl_2 \cdot NCl \cdot CO \cdot CH_3$ .*

This substance is prepared exactly as the last. It crystallises from light petroleum in small, short prisms melting at  $73^\circ$ .

0.2352 liberated  $I = 9.95$  c.c.  $N/10$  iodine.  $Cl$ , as  $:NCl$ , = 15.00.

$C_6H_3Cl_2 \cdot NCl \cdot CO \cdot CH_3$  requires  $Cl$ , as  $:NCl$ , = 14.87 per cent.

The isomeric change of this compound dissolved in acetic acid requires twelve days for completion. Repeated recrystallisation of the product from alcohol separated it into 2:4:5-trichloroacetanilide, and the hitherto unknown 2:3:6-trichloroacetanilide, which melts at  $134.5^\circ$ . The former is present in by far the larger proportion.

*Acetylchloramino-2:4:5-trichlorobenzene (2:4:5-Trichlorophenyl Acetyl Nitrogen Chloride),  $C_6H_2Cl_3 \cdot NCl \cdot CO \cdot CH_3$ .*

To a solution of the anilide in glacial acetic acid, excess of a solution of bleaching powder is added. An oil separates, which is dissolved in hot light petroleum. On cooling, rosettes of short, thick prisms form, melting at  $96^\circ$ .

0.3815 liberated  $I = 14.2$  c.c.  $N/10$  iodine.  $Cl$ , as  $:NCl$ , = 12.98.

$C_6H_2Cl_3 \cdot NCl \cdot CO \cdot CH_3$  requires  $Cl$ , as  $:NCl$ , = 12.99 per cent.

\* On analysis: 0.2175 gave 0.3917  $AgCl$ .  $Cl = 44.53$ .

$C_6H_2Cl_3 \cdot NH \cdot CO \cdot CH_3$  requires  $Cl = 44.60$  per cent.



This nitrogen chloride undergoes isomeric change only after heating in a sealed tube with glacial acetic acid at 150—170° for 2—3 hours. A considerable amount of hydrolysis accompanies the transformation into 2 : 3 : 4 : 6-tetrachloroacetanilide,\* the yield of which is accordingly small. The latter, after recrystallising from benzene, out of which it separates in glistening, flattened prisms, melts constantly at 181°, instead of at 174°, as given by Beilstein and Kurbatoff (*loc. cit.*).

*Acetylchloramino-2 : 3 : 4-trichlorobenzene* (2 : 3 : 4-*Trichlorophenyl Acetyl Nitrogen Chloride*),  $C_6H_2Cl_3 \cdot NCl \cdot CO \cdot CH_3$ .

This compound is prepared as the last. It crystallises in clusters of flattened prisms melting at 113—114°.

0.2543 liberated  $I = 9.35$  c.c.  $N/10$  iodine.  $Cl$ , as  $:NCl$ , = 13.03.

$C_6H_2Cl_3 \cdot NCl \cdot CO \cdot CH_3$  requires  $Cl$ , as  $:NCl$ , = 12.99 per cent.

The isomeric change is effected by heating in a sealed tube at 150—170°, and the yield of tetrachloroacetanilide is small. It is separated from regenerated trichloroacetanilide by recrystallising from benzene, in which the latter compound is much the more soluble.

*Acetylchloramino-2 : 3 : 6-trichlorobenzene* (2 : 3 : 6-*Trichlorophenyl Acetyl Nitrogen Chloride*),  $C_6H_2Cl_3 \cdot NCl \cdot CO \cdot CH_3$ .

This substance, which is prepared as the last, crystallises in well defined, four-sided, flattened prisms melting at 116°.

0.2402 liberated  $I = 8.8$  c.c.  $N/10$  iodine.  $Cl$ , as  $:NCl$ , = 12.98.

$C_6H_2Cl_3 \cdot NCl \cdot CO \cdot CH_3$  requires  $Cl$ , as  $:NCl$ , = 12.99 per cent.

It undergoes transformation into tetrachloroacetanilide, but much hydrolysis of the nitrogen chloride accompanies the isomeric change.

*Acetylchloramino-2 : 3 : 4 : 6-tetrachlorobenzene* (2 : 3 : 4 : 6-*Tetrachlorophenyl Acetyl Nitrogen Chloride*),  $C_6HCl_4 \cdot NCl \cdot CO \cdot CH_3$ .

This nitrogen chloride, prepared as the last, crystallises in clusters of small prisms and melts at 97°.

0.1671 liberated  $I = 10.42$  c.c.  $N/10$  iodine.  $Cl$ , as  $:NCl$ , = 11.05.

$C_6HCl_4 \cdot NCl \cdot CO \cdot CH_3$  requires  $Cl$ , as  $:NCl$ , = 11.54 per cent.

\* On analysis: 0.1489 gave 0.8139  $AgCl$ .  $Cl = 52.12$ .

$C_6HCl_4 \cdot NH \cdot CO \cdot CH_3$  requires  $Cl = 51.96$  per cent.

*Action of Bleaching Powder on a hot Acetic Acid solution of m-Chloroacetanilide.*

To a solution of *m*-chloroacetanilide in acetic acid, heated on the water-bath, a solution of bleaching powder was added until chlorine was evolved freely. An oily liquid separated consisting of a mixture of the nitrogen chlorides of the three trichloroacetanilides. To convert the nitrogen chlorides into the anilides, the oil was cautiously warmed with a little alcohol, and, after the reaction had taken place, sufficient alcohol was added to completely dissolve the solid. On cooling, crystals both of the 2:4:5- and the 2:3:4-trichloroacetanilides were deposited, and separated by fractional crystallisation from benzene or 50 per cent. acetic acid. The alcoholic mother liquor on evaporation yielded a solid, from which benzene extracted only a small amount of anilide, chiefly 2:3:4-trichloroacetanilide. The residue, insoluble in benzene, consisted of 2:3:6-trichloroaniline hydrochloride, which yields the base, melting at 70.5° on heating with water. In the treatment with alcohol, the nitrogen chloride of 2:3:6-trichloroacetanilide appears to decompose with formation of the aniline.

The chlorination of *m*-bromoacetanilide is being investigated, and so far derivatives have been obtained which behave in a manner analogous to those above described.

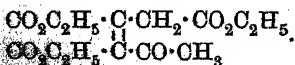
CHEMICAL LABORATORY,

ST. BARTHOLOMEW'S HOSPITAL AND COLLEGE, E.C.

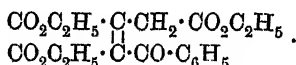
**LXXII.—Condensation of Ethyl Acetylenedicarboxylate with Bases and  $\beta$ -Ketonic Esters.**

By SIEGFRIED RUHEMANN and H. E. STAPLETON, B.A., Scholar of St. John's College, Oxford.

In a recent paper (Trans., 1900, 77, 242), we showed that *o*-phenylenediamine condenses with ethyl acetylenedicarboxylate to form ethyl quin-oxalidoneacetate, and it was concluded from this observation that in the condensation of ethyl acetylenedicarboxylate with ethyl acetate or ethyl benzoylacetate, both hydrogen atoms of the CH<sub>2</sub> group of the ketonic compounds play a part. The products would be respectively:

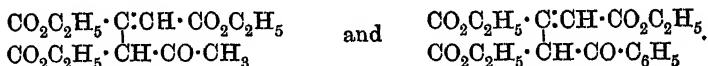


I. Ethyl acetoconitate.



II. Ethyl benzoylconitate.

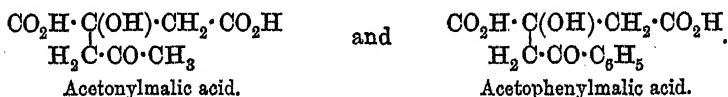
A comparison of properties has proved the identity of these esters with the substances previously obtained by the action of the sodium derivatives of the ketonic esters on ethyl chlorofumarate or chloromaleate (Trans., 1896, 69, 530, 1383; 1897, 71, 323). For the latter products, the following constitutional formulæ had been proposed from their mode of formation :



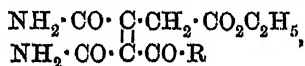
These expressions, however, do not account for the fact that ethyl chlorofumarate gives the same substance as ethyl chloromaleate, nor is it apparent from the formulæ why the esters do not give a coloration with ferric chloride.

Both these difficulties have been removed by the discovery that the esters in question are identical with those obtained from ethyl acetylenedicarboxylate and the ketonic esters, and that their constitution is to be expressed by formulæ I and II.

The alteration of the constitution assigned to the esters does not necessitate a change in the structure of the acids which result from their hydrolysis. These may still be expressed by the formulæ :

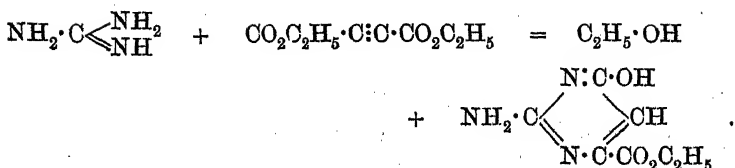


The compounds formed from the esters of acetoacetic and benzoylacetic acids and ammonia, however, are no longer to be regarded as cyclic in constitution. The products formed with aqueous ammonia (Trans., 1896, *loc. cit.*) are *diamides*, probably of the formula

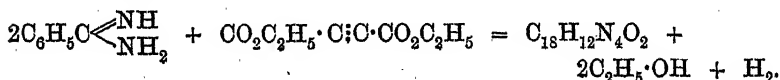


(R being  $\text{CH}_3$  or  $\text{C}_6\text{H}_5$ ), although the two  $\text{CO} \cdot \text{NH}_2$  groups may be differently distributed, whilst alcoholic ammonia gives *monamides*, for example, the monamide of ethyl benzoylacetic (previously called ethyl benzoyltrimethylenetricarboxylate, Ruhemann and Cunningham, Trans., 1899, 75, 785).

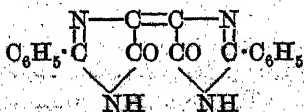
The difference in the behaviour of the ethyl esters of acetylenedicarboxylic and phenylpropionic acids, which had been established by previous experiments, as well as the results obtained by the interaction of ethyl phenylpropionate with bases, such as guanidine and benzamidine, induced us to similarly investigate the reactions of these bases with ethyl acetylenedicarboxylate. We find that guanidine readily condenses with this ester according to the following equation :



The product of the reaction is therefore to be regarded as *ethyl hydroxamidopyrimidinecarboxylate*. This view of the constitution of the substance is supported by the fact that it has both acidic and basic properties, and that when boiled with caustic potash hardly any decomposition takes place, apart from hydrolysis to the corresponding acid. Even more striking than the case of guanidine is the difference benzamidine exhibits towards ethyl phenylpropiolate and ethyl acetylenedicarboxylate. Whilst the former ester reacts with only 1 mol. of the base to form either benzalglyoxaldine or diphenylpyrimidone, the latter condenses with 2 mols. of benzamidine, according to the following equation :

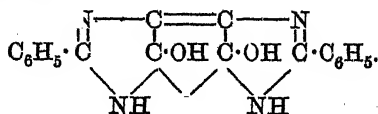


The hydrogen figuring in this equation seems to effect a reduction, thus diminishing the yield. The substance  $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_2$  forms ruby-red crystals, and probably has the constitution



It may be called *glyoxaline red*, and its formula indicates the close relationship it bears to indigotin and pyrazole blue.

Glyoxaline red suffers a remarkable change on boiling with glacial acetic acid: it takes up 1 mol.  $\text{H}_2\text{O}$  and is transformed into yellow needles of the composition  $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_3$ , for which we can only suggest the following structure :

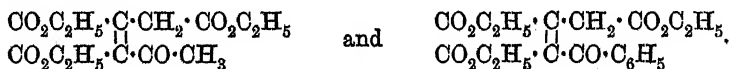


Finally, we show that ethyl chlorofumarate yields the same products with guanidine and benzamidine, as does ethyl acetylenedicarboxylate, and may be advantageously used in reactions in the place of the latter ester. This result is therefore analogous to that obtained by the study of the action of these esters on ethyl acetoacetate and ethyl benzoylacetate.

## EXPERIMENTAL.

*Ethyl Esters of Acetoaconitic and Benzoylaconitic Acids.*

The considerations which we brought forward in our last communication (*loc. cit.*) led to the conclusion that the compounds which are produced by the action of ethyl acetoacetate and benzoylacetate on ethyl acetylenedicarboxylate are not to be regarded as derivatives of trimethylene, but as the ethyl esters of acetoaconitic and benzoylaconitic acids :



This view is further supported by the determination of the molecular refraction of the ester obtained from ethyl acetoacetate, which Mr. O. W. Richardson, of Trinity College, kindly undertook for us. The following data,

$$\mu_{\text{Na}} = 1.469 ; d_{16^\circ/16^\circ} = 1.1580 ; M = 300,$$

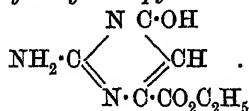
lead to the molecular refraction  $M \frac{\mu^2 - 1}{(\mu^2 + 2)d} = 72.11$ . This value corresponds to that calculated for the above formula, which requires 71.94.

We have pointed out in the introduction that these esters are identical with those which are formed by using ethyl chlorofumarate instead of ethyl acetylenedicarboxylate. This identity follows from their boiling points being the same, and also from their chemical behaviour. Both the esters which are formed from ethyl acetoacetate by its reaction with ethyl chlorofumarate and ethyl acetylenedicarboxylate yield with bromine the same substitution product, *ethyl bromoacetoconitate*,  $\text{C}_{14}\text{H}_{19}\text{O}_7\text{Br}$ . This is obtained by gradually adding bromine to a solution of the esters in chloroform, when hydrogen bromide is evolved, the reaction being accompanied by development of heat. The product is well shaken with water, the chloroform evaporated, and the residual oil, after drying with calcium chloride, distilled in a vacuum. It boils with only slight decomposition at  $214^\circ$  under a pressure of 18 mm., and has a specific gravity  $d_{7^\circ/7^\circ} = 1.4028$ . On analysis, the following numbers were obtained :

0.3107 gave 0.1559 AgBr. Br = 21.34.

0.3306 „ 0.1659 AgBr. Br = 21.35.

$\text{C}_{14}\text{H}_{19}\text{O}_7\text{Br}$  requires Br = 21.10 per cent.

*Ethyl Hydroxyaminopyrimidinecarboxylate,*

This compound is readily formed by mixing alcoholic solutions of guanidine thiocyanate and sodium ethoxide in molecular proportion, and then gradually adding the equivalent quantity of ethyl acetylenedicarboxylate. The reaction takes place with development of heat and formation of a brown coloration. After standing for a day, water is added to the mixture, when a reddish solution is produced. On acidifying this with acetic acid, a solid is precipitated, which can only be filtered with difficulty. It is sparingly soluble in boiling water and dissolves in a large quantity of hot alcohol, from which, after treatment with animal charcoal, it crystallises in small, yellowish needles, which begin to decompose at 220°. The compound was analysed, with the following results :

0.1727 gave 0.2915 CO<sub>2</sub> and 0.0775 H<sub>2</sub>O. C = 46.03 ; H = 4.98.

0.2055 ,, 40 c.c. of moist nitrogen at 10° and 755 mm. N = 23.14.

0.2020 ,, 39.5 c.c. ,, ,, 13° ,, 755 mm. N = 22.94.

C<sub>7</sub>H<sub>9</sub>O<sub>3</sub>N<sub>3</sub> requires C = 45.90 ; H = 4.91 ; N = 22.95 per cent.

The compound dissolves in cold dilute alkali, yielding a yellowish solution, and therefore possesses acidic properties. On the other hand, it has the character of a base, since it is readily soluble in concentrated hydrochloric acid. Platinic chloride precipitates from this solution yellowish needles of a *platinichloride*, which was analysed :

0.3 left, on ignition, 0.0752 Pt. Pt = 25.06.

(C<sub>7</sub>H<sub>9</sub>O<sub>3</sub>N<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>PtCl<sub>6</sub> requires Pt = 25.07 per cent.

The above constitution is in full agreement with the behaviour of the ester when boiled with a concentrated solution of caustic potash. Although some evolution of ammonia occurs, it suffers little decomposition, except hydrolysis, the larger portion being changed only to the corresponding *acid*, which is precipitated from the alkaline fluid by an excess of acetic acid. As hydroxyaminopyrimidinecarboxylic acid is very sparingly soluble in ordinary solvents, it is purified by boiling its solution in sodium carbonate with animal charcoal and adding acetic acid to the filtrate. A white powder is thus obtained which does not melt, but begins to blacken above 320°.

On analysis, the following numbers were obtained :

0.2190 gave 0.3163  $\text{CO}_2$  and 0.0710  $\text{H}_2\text{O}$ .  $\text{C} = 39.38$ ;  $\text{H} = 3.60$ .

0.2234 „ 0.3155  $\text{CO}_2$  „ 0.0750  $\text{H}_2\text{O}$ .  $\text{C} = 38.51$ ;  $\text{H} = 3.70$ .

0.2130 „ 49.5 c.c. moist nitrogen at  $15^\circ$  and 750 mm.  $\text{N} = 26.83$ .

$\text{C}_6\text{H}_5\text{O}_3\text{N}_3$  requires  $\text{C} = 38.71$ ;  $\text{H} = 3.22$ ;  $\text{N} = 27.09$  per cent.

The solution of the acid in ammonia gives a gelatinous silver salt. The acid, like its ester, has basic properties, dissolving in hot concentrated hydrochloric acid, and from the solution, on cooling, colourless crystals of the hydrochloride separate out. This salt, however, is unstable, and loses hydrochloric acid, not only at  $100^\circ$ , but even at the ordinary temperature.

The same ester is obtained from guanidine by using ethyl chlorofumarate instead of ethyl acetylenedicarboxylate, and this is, indeed, a preferable method of preparing the substance. Its identity with ethyl hydroxyaminopyrimidinecarboxylate was verified by a direct comparison of their properties and by the following nitrogen determination :

0.206 gave 40.5 c.c. moist nitrogen at  $13^\circ$  and 756 mm.  $\text{N} = 23.1$ .

$\text{C}_7\text{H}_9\text{O}_3\text{N}_3$  requires  $\text{N} = 22.95$  per cent.

*Action of Benzamidine on the Ethyl Esters of Acetylenedicarboxylic and Chlorofumaric Acids. Formation of Glyoxaline Red,  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_4$ .*

The interesting behaviour of benzamidine towards ethyl phenylpropiolate, which yields, according to the temperature at which the reaction is allowed to proceed, either benzalglyoxalidone or diphenylpyrimidone, induced us to study the reaction of benzamidine, on the one hand with ethyl acetylenedicarboxylate, and on the other with ethyl chlorofumarate. We have found that the same compound results from either ester.

The reaction is effected by mixing alcoholic solutions of sodium ethoxide and benzamidine hydrochloride, and gradually adding ethyl acetylenedicarboxylate or ethyl chlorofumarate. The mixture, which first turns yellow and finally becomes dark red, is allowed to stand for a day; water and a little acetic acid are then added, and the red solid collected. This is insoluble in water, but dissolves, although with great difficulty, in a large amount of boiling alcohol, and, on cooling, gradually separates out in ruby-red crystals. The yield is unsatisfactory, this being partly due to the circumstance that reduction accompanies the formation of the substance. The compound dissolves in alkali, yielding a red solution, and therefore has acidic properties.

The following analytical data were obtained :

0.3024 gave 0.7550  $\text{CO}_2$  and 0.1092  $\text{H}_2\text{O}$ .  $\text{C} = 68.08$ ;  $\text{H} = 4.0$ .

0.1550 „ 0.3888  $\text{CO}_2$  „ 0.0598  $\text{H}_2\text{O}$ .  $\text{C} = 68.41$ ;  $\text{H} = 4.27$ .

0.1933 „ 28 c.c. moist nitrogen at  $13^\circ$  and 772 mm.  $\text{N} = 17.40$

$\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_4$  requires  $\text{C} = 68.35$ ;  $\text{H} = 3.80$ ;  $\text{N} = 17.72$  per cent.

On boiling with glacial acetic acid, glyoxaline red suffers a remarkable change; it enters into solution and, on cooling, yellowish needles separate out, which decompose at  $262^{\circ}$ .

The analytical results obtained with different specimens proves the substance to have the composition  $C_{18}H_{14}O_3N_4$ , which differs from that of glyoxaline red by the elements of 1 mol.  $H_2O$ .

0.2040 gave 0.4820  $CO_2$  and 0.0790  $H_2O$ . C = 64.55; H = 4.30.

0.2093 „ 0.4935  $CO_2$  „ 0.0806  $H_2O$ . C = 64.30; H = 4.27.

0.2255 „ 0.5330  $CO_2$  „ 0.0875  $H_2O$ . C = 64.46; H = 4.31.

0.1490 „ 21.5 c.c. moist nitrogen at  $20^{\circ}$  and 757 mm. N = 16.43.

0.1982 „ 27 c.c. „ „  $10^{\circ}$  „ 779 mm. N = 16.76.

0.2144 „ 31 c.c. „ „  $16^{\circ}$  „ 750 mm. N = 16.63.

$C_{18}H_{14}O_3N_4$  requires C = 64.67; H = 4.19; N = 16.76 per cent.

The close relation of this compound to the red product follows, not only from its mode of formation, but also from the fact that its yellow solution in dilute potash quickly changes on standing to reddish-violet the colour of the alkaline solution of glyoxaline red.

An attempt to support the constitutional formulæ of both substances (p. 806) by means of their behaviour towards boiling caustic potash has furnished the following result. The solution darkens, and an evolution of ammonia takes place, which ceases after about an hour's heating. The alkaline liquid is freed by filtration from a small quantity of a brown precipitate, then acidified with hydrochloric acid and extracted with ether. This dissolves out a solid which we have identified as benzoic acid. Besides this acid and ammonia, there is also formed oxalic acid. These decomposition products agree with the formulæ of the compounds given in the introduction, but it is obvious that further experiments are desirable before the formulæ can be regarded as conclusively established.

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### LXXIII.—*Bromination of Benzeneazophenol. Part II.*

By JOHN THEODORE HEWITT and WILLIAM GEORGE ASTON.

It has been recently shown by the authors that when benzeneazophenol is brominated in a glacial acetic acid solution containing excess of fused sodium acetate, two bromine atoms enter the phenol nucleus in the ortho-position relatively to the hydroxyl group (Trans., 1900, 77, 712). In the absence of sodium acetate, a bromo-derivative of unknown constitution was obtained, the investigation of which forms the subject of the present communication.



*p*-Bromobenzeneazodibromophenol.

When benzeneazophenol is dissolved in five times its weight of glacial acetic acid and treated with one molecular proportion of bromine, only a portion of the azophenol is attacked, for on pouring into water, collecting the precipitate, and recrystallising it a few times from glacial acetic acid, a compound is isolated which is sparingly soluble in cold acetic acid and melts at 143—145° (uncorr.). The various preparations were found to contain a percentage of bromine corresponding with that required for the formula  $C_{12}H_7ON_2Br_3$ .

Experiments were then made on the bromination of benzeneazophenol suspended in water, molecular proportions being again employed, but the same brominated product was obtained, although, owing to the reaction not having proceeded so smoothly as in acetic acid solution, the melting point was generally a degree or two lower.

Finally, it was found that a satisfactory yield of the substance might be obtained by the following procedure. Ten grams of finely powdered benzeneazophenol are suspended in 50 grams of glacial acetic acid, the mixture being well cooled by ice, and stirred while 25 grams of bromine diluted with 25 grams of glacial acetic acid are gradually added. The bromine is used up rapidly, and only a trace of it can be detected at the end of the operation if the above quantities are employed. The product is poured into water, the precipitate collected, washed, and recrystallised from glacial acetic acid. The brownish-orange needles so obtained were analysed with the following result:

0.1743 gave 0.2125  $CO_2$  and 0.0331  $H_2O$ .  $C = 33.25$ ;  $H = 2.11$ .

0.1924 „ 0.2489 AgBr.  $Br = 55.04$ .

0.2603 „ 15.6 c.c. moist nitrogen at 18° and 766 mm.  $N = 7.27$ .  
 $C_{12}H_7ON_2Br_3$  requires  $C = 33.10$ ;  $H = 1.63$ ;  $Br = 55.14$ ;  $N = 6.45$  percent.

The substance melts at 148° (corr.), and dissolves in acetone, ethyl alcohol, ethyl acetate, benzene or its homologues, aniline or nitrobenzene; it is less soluble in cold glacial acetic acid, and dissolves very sparingly in light petroleum. On treatment with concentrated sulphuric acid, the substance yields a dark red sulphate of the corresponding quinonehydrazone, the azophenol separating as a yellow precipitate on the addition of water.

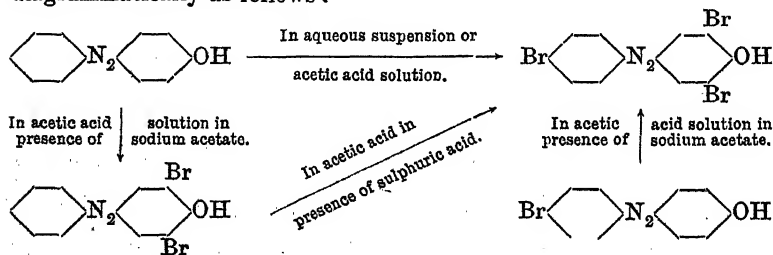
Conclusive evidence in favour of the view that the substance is *p*-bromobenzeneazodibromophenol was obtained by brominating *p*-bromobenzeneazophenol in presence of sodium acetate, and benzeneazo-*o*-dibromophenol in presence of strong sulphuric acid. The same substance was obtained in both cases, and proved to be identical with the product obtained by the direct action of bromine on benzene-

azophenol; each preparation causing no depression of the melting point of the others.

*Bromination of Benzeneazodibromophenol.*—Twenty-four grams of benzeneazodibromophenol were suspended in 290 grams of glacial acetic acid mixed with 24 grams of concentrated sulphuric acid, and to the well cooled mixture, 11 grams of bromine, diluted with 44 grams of glacial acetic acid, were slowly added. The product was recrystallised from acetone, and melted at  $148^{\circ}$ .

*Bromination of p-Bromobenzeneazophenol.*—1.3 grams of *p*-bromobenzeneazophenol were dissolved in 50 grams of acetic acid together with 1.3 grams of fused sodium acetate. The solution was well cooled, and 1.5 grams of bromine in 4 grams of acetic acid added. The product, after recrystallisation, melted at  $148^{\circ}$ .

The production of *p*-bromobenzeneazo-*o*-dibromophenol can be shown diagrammatically as follows:



The *acetyl* derivative was obtained by boiling *p*-bromobenzeneazodibromophenol for 1 hour with an equal weight of fused sodium acetate and three times its weight of acetic anhydride. It separates from glacial acetic acid in very small crystals, but in larger, orange prisms from chloroform in which it is easily soluble. The melting point is  $167^{\circ}$ .

0.1460 gave 0.1883  $\text{CO}_2$  and 0.0359  $\text{H}_2\text{O}$ .  $\text{C} = 35.17$ ;  $\text{H} = 1.97$ .

$\text{C}_{14}\text{H}_9\text{O}_2\text{N}_2\text{Br}_3$  requires  $\text{C} = 35.22$ ;  $\text{H} = 1.89$  per cent.

The compound is very soluble in carbon disulphide and moderately so in aniline, benzene, toluene, nitrobenzene, ethyl ether, ethyl acetate, or ethyl benzoate, but dissolves only sparingly in cold acetone, amyl or ethyl alcohol, or light petroleum.

The *benzoyl* derivative was prepared by boiling the azophenol for 1 hour with  $2\frac{1}{2}$  times its weight of benzoyl chloride, and was recrystallised from a large excess of spirit, in which, even at the boiling point, it is but very sparingly soluble. It forms brownish-orange needles melting at  $129^{\circ}$ .

0.2188 gave 13.4 c.c. moist nitrogen at  $16^{\circ}$  and 750 mm.  $\text{N} = 6.00$ .

$\text{C}_{19}\text{H}_{11}\text{O}_2\text{N}_2\text{Br}_3$  requires  $\text{N} = 5.21$  per cent.

The substance is taken up sparingly by acetic acid, ethyl alcohol, or petroleum spirit; it is fairly easily soluble in carbon disulphide, benzene or its homologues, or aniline, whilst in the remaining organic solvents its solubility is moderate.

The *ethyl ester* was obtained by heating 5 grams of the azophenol with 0.7 gram of caustic potash, 1.6 grams of ethyl bromide, and about 50 c.c. of absolute alcohol in a sealed tube for  $1\frac{1}{2}$  hours at  $105-110^\circ$ . After cooling, the contents of the tube were warmed on the water-bath with dilute caustic soda, the insoluble ethyl ether collected, washed, dried, and recrystallised from benzene. Beautiful, golden needles melting at  $125^\circ$  were obtained, which were very soluble in carbon disulphide and dissolved fairly easily in ether, ethyl benzoate, or hydrocarbon solvents. The solubility in acetone, ethyl alcohol, or amyl alcohol was slight.

0.1027 gave 0.1361  $\text{CO}_2$  and 0.0203  $\text{H}_2\text{O}$ .  $\text{C} = 36.14$ ;  $\text{H} = 2.20$ .

$\text{C}_{14}\text{H}_{11}\text{ON}_2\text{Br}_3$  requires  $\text{C} = 36.28$ ;  $\text{H} = 2.40$  per cent.

*Tribromobenzeneazophenol*.—As it seemed at one time possible that the substance obtained by the direct action of bromine on benzeneazophenol might be tribromobenzeneazophenol, the latter was synthetically prepared by coupling diazotised tribromoaniline with phenol. The only azo-compound derived from tribromoaniline, so far as the authors know, is the tribromobenzeneazodimethylaniline described by Silberstein (*J. pr. Chem.*, 1883, [ii], 27, 113). Since Silberstein's method of diazotising tribromoaniline is rather tedious, the process we adopted may be described, as it is simple. 13.2 grams of finely powdered tribromoaniline were dissolved in 15 c.c. of concentrated sulphuric acid, a finely divided precipitate of the base or its sulphate being obtained by the addition of 5 c.c. of water. The well-cooled mixture was diazotised by adding 2.8 grams of pure, solid sodium nitrite in small portions at a time, left for 2 hours, and then poured on to crushed ice. Ten minutes later, the solution was added to 4 grams of phenol and 40 grams of sodium carbonate, ( $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), dissolved in 300 c.c. of water and cooled to  $-1^\circ$ . The precipitated azo-compound was collected, washed, and extracted with hot dilute caustic potash solution, the filtrate precipitated by hydrochloric acid and the azophenol recrystallised from glacial acetic acid. Small, bright, orange prisms were obtained melting at  $168.5^\circ$ .

0.2627 gave 0.3229  $\text{CO}_2$  and 0.0382  $\text{H}_2\text{O}$ .  $\text{C} = 33.41$ ;  $\text{H} = 1.68$ .

$\text{C}_{12}\text{H}_7\text{ON}_2\text{Br}_3$  requires  $\text{C} = 33.10$ ;  $\text{H} = 1.63$  per cent.

Tribromobenzeneazophenol is easily soluble in acetone or ethyl acetate, dissolves fairly well in ethyl alcohol, ethyl ether, acetic acid, or benzene, but is only very sparingly soluble in light petroleum. For

further characterisation, the acetyl and benzoyl derivatives were prepared.

*Acetyl Derivative.*—The acetylation was carried out with fused sodium acetate and acetic anhydride, and the substance recrystallised from glacial acetic acid. Thus obtained, it forms small, red, radiating groups melting at 105°.

0.2462 gave 13.5 c.c. moist nitrogen at 12° and 762 mm.  $N = 6.54$ .

$C_{14}H_9O_2N_2Br_3$  requires  $N = 5.89$  per cent.

The *benzoyl* derivative was obtained by the Schotten-Baumann method and recrystallised from boiling amyl alcohol in which it is not very soluble.

0.2704 gave 12.3 c.c. moist nitrogen at 12° and 762 mm.  $N = 5.41$ .

$C_{19}H_{11}Br_3O_2N_2$  requires  $N = 5.21$  per cent.

It is an orange-pink, crystalline powder which, as seen under the microscope, consists of radiating groups of very small prisms. It melts at 132° and is very sparingly soluble in the usual solvents.

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## LXXIV.—*Action of Formaldehyde on Amines of the Naphthalene Series. Part II.*

By GILBERT THOMAS MORGAN, D.Sc.

In a former paper on this subject (Trans., 1898, 73, 536), an account was given of the interactions occurring, under various conditions, between formaldehyde and  $\beta$ -naphthylamine. The results showed that the chemical changes involved are somewhat complex, and differ considerably from those produced when this aldehyde is condensed with benzenoid amines.

In order to obtain further evidence as to the nature of these reactions, a series of comparative experiments has been made with derivatives of  $\beta$ -naphthylamine, the object being so to regulate the action of the aldehyde that products could be isolated corresponding with each of the phases in the condensations of this reagent with the parent base.

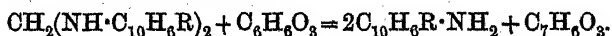
When  $\beta$ -naphthylamine is condensed with formaldehyde in cold alcoholic or acetic acid solution, 2 : 2'-dimethylenediamino-1 : 1'-dinaphthylmethane is produced, 3 mols. of the aldehyde combining with 2 mols. of the base and 3 mols. of water being eliminated (*loc. cit.*, 550). The substance isolated is in all probability the final product of

a succession of molecular rearrangements, for compounds of the simpler type  $\text{CH}_2(\text{NHR})_2$  have been obtained with the halogen derivatives of  $\beta$ -naphthylamine. 2:2'-Dimethylenediamino-1:1'-dinaphthylmethane, when heated with concentrated hydriodic acid and red phosphorus, yields naphthacridine, and this result not only shows that the diamine contains one methylene group attached to two aromatic nuclei, but also that the positions of attachment of the linking carbon atom are the same in both compounds.

Although the orientation of the meso-carbon atom present in these bases has not been established either by direct synthesis or by reference to some naphthalene derivative of known constitution, yet the fact, that, in the formation of homonucleol derivatives of  $\beta$ -naphthylamine, substitution invariably occurs in the contiguous  $\alpha$ -, and not in the second  $\beta$ -position, is a strong argument in favour of the constitution generally assigned to naphthacridine.

Further confirmatory evidence has been obtained by a study of the behaviour of 1-bromo-2-naphthylamine and its chlorine analogue towards formaldehyde. These bases, when treated with this reagent in cold glacial acetic acid, yield methylene derivatives containing the radicle solely attached to nitrogen, *methylenedi-1-bromo-2-naphthylamine*,  $\text{CH}_2(\text{NH}\cdot\text{C}_{10}\text{H}_7\text{Br})_2$ , being obtained from 1-bromo-2-naphthylamine and *methylene di-1-chloro-2-naphthylamine*,  $\text{CH}_2(\text{NH}\cdot\text{C}_{10}\text{H}_7\text{Cl})_2$ , from the corresponding chloro-compound. In a preliminary note on the action of formaldehyde on substituted  $\beta$ -naphthylamines (Proc., 1899, 15, 10), these substances were described as having the constitutional formulæ,  $\text{CH}_2\cdot\text{N}\cdot\text{C}_{10}\text{H}_7\text{Br}$  and  $\text{CH}_2\cdot\text{N}\cdot\text{C}_{10}\text{H}_7\text{Cl}$ . A more detailed examination, however, has shown that each contains a methylene group attached to two nitrogen atoms.

Anhydro-bases of the type  $\text{RCH}\cdot\text{NX}$  are unsaturated compounds, and combine additively with hydrogen cyanide (von Miller and Plöchl, *Ber.*, 1896, 29, 1729; Eibner, *Annalen*, 1898, 302, 313), whereas the above compounds are not affected by this reagent. When boiled with dilute mineral acids, these methylene bases are hydrolysed into their generators, a certain amount of resinous bye-product being simultaneously formed in the case of the bromo-compound. The methylene group may, however, be quantitatively eliminated by a modification of the method employed by Clowes and Tollens in the estimation of this radicle in the methylene derivatives of the sugar series (*Ber.*, 1899, 32, 2841). When warmed at  $70^\circ$  with excess of phloroglucinol dissolved in glacial acetic acid, the anhydro-base decomposes in accordance with the following equation:



On diluting the solution with water, the insoluble phloroglucide:

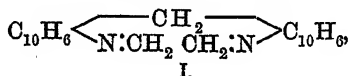
$(C_7H_6O_3)_x$ , is completely precipitated, whilst the regenerated amine remains dissolved, and is easily identified in the filtrate.

These anhydro-bases are the first compounds of the type  $CH_2(NHR)_2$  in the naphthalene series. Methylenedi-1-chloro-2-naphthylamine is quite stable in warm glacial acetic acid, and is not transformed into a dinaphthylmethane base when heated with 1-chloro-2-naphthylamine and its hydrochloride.

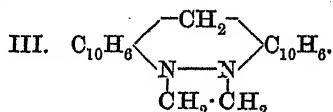
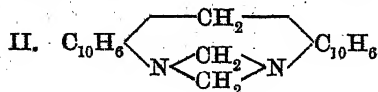
Methylenedi-1-bromo-2-naphthylamine resembles its chlorine analogue, but is far less stable. It gradually decomposes, yielding a red, resinous substance when heated to  $90^\circ$  either alone or in solution.

These results indicate that the migration of methylene into the naphthalene nucleus is prevented by the presence of substituent radicals in the  $\alpha$ -position contiguous to the amino-group, and confirm the assumption made with reference to the position of the meso-carbon atom of naphthacridine and 2:2'-dimethylenediamino-1:1'-dinaphthylmethane.

The latter base contains, in addition, two other methylene radicals attached to the nitrogen atoms, and although the formula,

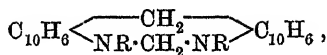


suggested for this substance in the former communication indicates its mode of formation, and also expresses its tertiary character, yet, in view of the fact that the nitrogen atoms are in the ortho-position relatively to the third methylene group, and therefore in close proximity to each other, it is quite conceivable that a rearrangement of the valencies may occur, giving rise to a molecular structure represented by one or other of the following formulæ:

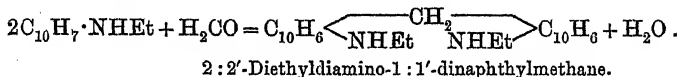


It might reasonably be supposed that a base containing two  $N:CH_2$  groups, as indicated by formula I, would be hydrolysed by dilute mineral acids, and reduced by sodium and amyl alcohol; it should also combine additively with hydrogen cyanide. The base, however, is not affected by these reagents, and its stability is a point in favour of the view that rearrangement has taken place.

The substance indicated by formula II should also undergo hydrolysis, since the methylene groups are each attached to two nitrogen atoms, and, moreover, if any tendency exists for the linking up of the nitrogen atoms by methylene, in the manner suggested by formula II, it should be possible to obtain a compound of the type



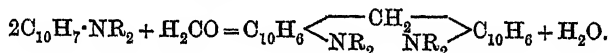
by the action of formaldehyde on a monoalkyl derivative of  $\beta$ -naphthylamine. When ethyl- $\beta$ -naphthylamine is treated in this way, 1 mol. only of formaldehyde interacts with 2 mols. of the amine, the product being a secondary base formed according to the equation



No further addition of methylene occurs, even when excess of the aldehyde is employed. As the linking up of the nitrogen atoms by methylene does not occur in this case, it is improbable that the condensation product from  $\beta$ -naphthylamine has a constitution corresponding with II.

The formula III gives a satisfactory explanation of the behaviour of the substance towards hydrolytic and reducing agents. With regard to the action of hydriodic acid and red phosphorus, it will be noticed that the nitrogen atoms now form part of a seven-membered closed chain, and the production of naphthacridine may be expressed as a disruption of this unstable system, giving rise to the stable six-membered ring of the acridine type.

Formaldehyde condenses with tertiary  $\beta$ -naphthylamine derivatives in accordance with the equation



This reaction was found to occur in the case of dimethyl- $\beta$ -naphthylamine, diethyl- $\beta$ -naphthylamine, and dibenzyl- $\beta$ -naphthylamine. In each case, condensation was effected in glacial acetic acid, and it was noticed that the heat developed by the reaction diminishes as the hydrogen atoms of the amino-group of the parent base are successively replaced by alkyl radicles. The reaction with  $\beta$ -naphthylamine is extremely vigorous, and the mixture must be cooled in a freezing mixture to prevent the formation of tarry products; in the case of ethyl- $\beta$ -naphthylamine, there is an appreciable rise of temperature, but the action is so far under control that no external cooling is needed, the condensation with diethyl- $\beta$ -naphthylamine proceeds very slowly at the ordinary temperature, and it is therefore advisable either to apply heat or to add a dehydrating agent such as acetic anhydride.

The diphenylmethane bases containing the amino-group in the para-position, relatively to the methane carbon atom, are readily oxidised into colouring matters, whereas the dinaphthylmethane compounds, produced from  $\beta$ -naphthylamine and its alkyl derivatives, do not yield coloured substances when submitted to this treatment.

Dimethyl- $\alpha$ -naphthylamine was also condensed with formaldehyde in order to see whether a change in the orientation of the aminic nitrogen would affect this result; the product was a dinaphthylmethane base,  $\text{CH}_2(\text{C}_{10}\text{H}_7\cdot\text{NMe}_2)_2$ , which, like its  $\beta$ -isomeride, gave no colour reaction with lead peroxide. Friedländer and Welmans prepared the corresponding phenyldinaphthylmethane base from dimethyl- $\alpha$ -naphthylamine and benzaldehyde, and obtained a similar negative result with this oxidising agent (*Ber.*, 1888, 21, 3123).

Since the methylene and benzylidene groups invariably enter the ring in accordance with the "para-ortho" law, it follows that the condensation products from dimethyl- $\alpha$ -naphthylamine may have one of three constitutions; they may be either  $\alpha\alpha$ -(dipara),  $\alpha\beta$ -(paraortho), or  $\beta\beta$ -(diortho)-dinaphthylmethane derivatives. The non-formation of a coloured oxidation product seems to indicate that the bases are  $\beta\beta$ -compounds, containing both aminic nitrogen atoms in the ortho-position relatively to the methane carbon atom, but, although this fact would be conclusive evidence in the benzene series, yet it cannot be accepted as final in the case of these naphthalenoid derivatives, inasmuch as colouring matters of the rosaniline type containing only naphthalene nuclei have never been obtained, and it is therefore probable that the nature of the aromatic residue attached to the central carbon atom plays an important part in modifying the behaviour of the compound towards oxidising agents.

Naphthacridine is produced from  $\beta$ -naphthylamine and formaldehyde when the condensation takes place in the presence of mineral acids, a labile isomeride, isonaphthacridine, being formed as an intermediate product.

The production of an acridine base in one operation—a change involving simultaneous oxidation and the elimination of ammonia—is peculiar to  $\beta$ -naphthylamine; in the benzene series, the intermediate products can usually be isolated, owing to their greater stability. *m*-Toluylenediamine, for example, when condensed with formaldehyde, yields a tetraminodiphenylmethane containing two amino-groups in the ortho-position relatively to methylene; this base is quite stable, and only loses ammonia on digesting with acids, the product being the leuco-base of acridine yellow, which furnishes the colouring matter by subsequent oxidation (Leonhardt, D. R.-P, 52324, 70935).

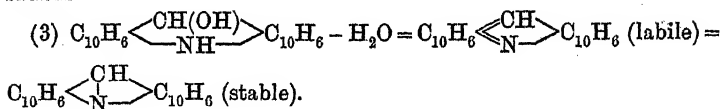
The formation of naphthacridine may be represented as taking place in the following stages:

(1)  $2\text{C}_{10}\text{H}_7\cdot\text{NH}_2 + \text{H}_2\text{CO} = \text{C}_{10}\text{H}_6\left\langle\begin{smallmatrix}\text{CH}_2 \\ \text{NH}\end{smallmatrix}\right\rangle\text{C}_{10}\text{H}_6 + \text{NH}_3 + \text{H}_2\text{O}$ , the dihydronaphthacridine (unstable) at once becoming oxidised.

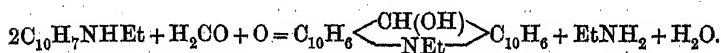
(2)  $\text{C}_{10}\text{H}_6\left\langle\begin{smallmatrix}\text{CH}_2 \\ \text{NH}\end{smallmatrix}\right\rangle\text{C}_{10}\text{H}_6 + \text{O} = \text{C}_{10}\text{H}_6\left\langle\begin{smallmatrix}\text{CH}(\text{OH}) \\ \text{NH}\end{smallmatrix}\right\rangle\text{C}_{10}\text{H}_6$  (unstable),



and the intermediate oxidation product undergoing further condensation.



When ethyl- $\beta$ -naphthylamine is substituted for  $\beta$ -naphthylamine in this reaction, 2 mols. of the base condense with 1 of the aldehyde, and ethylamine is eliminated instead of ammonia. The product contains oxygen, and has the composition  $\text{C}_{23}\text{H}_{19}\text{ON}$ . The analytical data point to its being an ethyl derivative of the intermediate oxidation product of dihydronaphthacridine, and this view of its constitution is in accordance with the mode of formation



*ar*-Tetrahydrodiethyl- $\beta$ -naphthylamine, which, according to Bamberger's researches, must be regarded as a benzenoid amine, does not react with formaldehyde under the conditions employed in the formation of 2 : 2'-tetraethyldiamino-1 : 1'-dinaphthylmethane. The methylene group shows very little tendency to take up the ortho-position relatively to an amino-radicle in the nucleus of a benzenoid amine, only a very small yield of the ditolylmethane base,  $\text{CH}_2(\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2)_2$  [Me :  $\text{CH}_2$  :  $\text{NH}_2$  = 1 : 3 : 4], being obtained by the intramolecular rearrangement of methylenedi-*p*-toluidine (Eberhardt and Welter, *Ber.*, 1894, 27, 1804). The reactivity of the hydrogen atom in the contiguous  $\alpha$ -position is a property of  $\beta$ -naphthylamine, and disappears when the naphthalenoid character of the aromatic nucleus is destroyed.

## EXPERIMENTAL.

### *Preparation of 1-Bromo-2-naphthylamine.*

Lellmann and Schmidt brominated aceto- $\beta$ -naphthalide dissolved in 50 per cent. acetic acid (*Ber.*, 1887, 20, 2154), but the recrystallised acetyl compound is so insoluble in this medium that it was found more convenient to dissolve it in glacial acetic acid.

The following method was found to give a good yield of 1-bromo-2-acetonaphthalide. Aceto- $\beta$ -naphthalide (30 grams) was dissolved in 7 parts of glacial acetic acid, and the theoretical quantity of bromine (26 grams) dissolved in 2 parts of the same solvent slowly added. The mixture was agitated continuously, and after the addition of the bromine, the precipitate of 1-bromo-2-acetonaphthalide was collected, washed with glacial acetic acid, dissolved in alcohol, and hydrolysed by boiling with concentrated hydrochloric acid until the

precipitation of 1-bromo-2-naphthylamine hydrochloride was complete. The base, obtained by decomposing the hydrochloride with caustic soda, was repeatedly crystallised from light petroleum, and separated in colourless needles melting at 63°.

*Action of Formaldehyde on 1-Bromo-2-naphthylamine. Methylenedi-1-bromo-2-naphthylamine.*

1-Bromo-2-naphthylamine dissolved in four times its weight of glacial acetic acid was treated with excess of formaldehyde solution. There was no apparent change, and no rise of temperature was observed, but on diluting the solution with water, a white precipitate was obtained which melted above 100°. The substance, which was produced with equal readiness by the addition of formaldehyde solution to an alcoholic solution of 1-bromo-2-naphthylamine, was recrystallised from alcohol, when the melting point rose to 141—143°. It was soon noticed that the new compound was somewhat unstable in character, for its solution in alcohol, benzene, or chloroform darkened on boiling, and a red, resinous substance was precipitated. Great care had to be exercised in order to obtain a colourless specimen. A portion of the substance, dried on porous plates, was finely powdered and added to benzene heated nearly to boiling; the substance rapidly dissolved, and the solution was filtered into a vessel provided with a tightly fitting stopper, and allowed to cool. The compound crystallised in colourless needles with a silky lustre, and melted at 145°.

0.2011 gave 0.4118 CO<sub>2</sub> and 0.0674 H<sub>2</sub>O. C=55.84; H=3.72.

0.1200 „ 0.2432 CO<sub>2</sub> „ 0.0438 H<sub>2</sub>O. C=55.27; H=4.05.

0.1878 „ 0.1530 AgBr. Br=34.67.

0.1453 „ 8.1 c.c. moist nitrogen at 22° and 765 mm. N=6.35.

C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>Br<sub>2</sub> requires C=55.26; H=3.51; Br=35.08; N=6.14 per cent.

When heated for a short time at 90°, the colourless, silky needles become reddened, and the same change takes place more slowly when the crystals are exposed to light.

*Methylenedi-1-bromo-2-naphthylamine*, CH<sub>2</sub>(NH·C<sub>10</sub>H<sub>6</sub>Br)<sub>2</sub>, when warmed with dilute acids, is partly hydrolysed into its generators, formaldehyde and 1-bromo-2-naphthylamine; at the same time, a portion is decomposed, yielding the resinous product previously mentioned.

A weighed quantity of the anhydro-base (0.4—0.7 gram) was suspended in 12 c.c. of a glacial acetic acid solution of phloroglucinol, and heated at 70° for about 2 hours, the solution was then diluted with an equal bulk of water and the precipitated phloroglucide collected in a Gooch crucible, dried at 110—120°, and weighed.

0.4428 gave 0.1033 phloroglucide.  $\text{CH}_2 = 2.35$ .

0.7273 „ 0.2369 „  $\text{CH}_2 = 3.25$ .

$\text{CH}_2(\text{C}_{10}\text{H}_6\text{Br})_2$  requires  $\text{CH}_2 = 2.82$  per cent.

The regenerated 1-bromo-2-naphthylamine was obtained by rendering the filtrates ammoniacal; after crystallisation from light petroleum it melted at  $60^\circ$  (corr.  $63^\circ$ ).

#### *Preparation of 1-Chloro-2-naphthylamine.*

Cleve states that 1-chloro-2-acetonaphthalide is produced by passing one molecular proportion of chlorine into a solution of aceto- $\beta$ -naphthalide in dilute acetic acid. Recrystallised aceto- $\beta$ -naphthalide is almost insoluble in dilute acetic acid, and it was found impossible to obtain a clean product by using this method. Chlorination by means of sulphuryl chloride did not lead to very satisfactory results.

I am indebted to Dr. Wynne for the details of the following method. A solution of 110 grams of aceto- $\beta$ -naphthalide in 1800 grams of glacial acetic acid was heated at  $45$ – $50^\circ$ , and chlorine was passed in until the increase in weight corresponded with the addition of one molecular proportion of the gas. The 1-chloro-2-acetonaphthalide, which separated during the action, was collected, recrystallised from alcohol, and hydrolysed by boiling with excess of hydrochloric acid in alcoholic solution. The hydrochloride of 1-chloro-2-naphthylamine, precipitated on cooling the alcoholic solution, was decomposed with caustic soda; the base, after repeated crystallisation from light petroleum, separated in colourless needles melting at  $60^\circ$ .

#### *Action of Formaldehyde on 1-Chloro-2-naphthylamine. Methylenedi-1-chloro-2-naphthylamine.*

*Methylenedi-1-chloro-2-naphthylamine*,  $\text{CH}_2(\text{NH}\cdot\text{C}_{10}\text{H}_6\text{Cl})_2$ , was prepared in a precisely similar manner to the bromo-derivative just described, by the action of formaldehyde on 1-chloro-2-naphthylamine in alcoholic or glacial acetic acid solution. The compound crystallises from chloroform or benzene in colourless needles with a silky lustre. It melts at  $179$ – $180^\circ$ . A specimen, crystallised from chloroform, was analysed with the following results:

0.1907 gave 0.4816  $\text{CO}_2$  and 0.0821  $\text{H}_2\text{O}$ .  $\text{C} = 68.87$ ;  $\text{H} = 4.78$ .

0.1447 „ 0.1153  $\text{AgCl}$ .  $\text{Cl} = 19.71$ .

0.1502 „ 10.3 c.c. moist nitrogen at  $15^\circ$  and 768 mm.  $\text{N} = 7.98$ .

With another specimen, crystallised from benzene, the following numbers were obtained:

0.1520 gave 0.3831  $\text{CO}_2$  and 0.0681  $\text{H}_2\text{O}$ .  $\text{C} = 68.60$ ;  $\text{H} = 4.98$ .

0.1514 „ 0.1194  $\text{AgCl}$ .  $\text{Cl} = 19.50$ .

$\text{C}_{21}\text{H}_{16}\text{N}_2\text{Cl}_2$  requires  $\text{C} = 68.66$ ;  $\text{H} = 4.37$ ;  $\text{Cl} = 19.34$ ;  $\text{N} = 7.63$  percent.

In outward appearance, this compound closely resembles the bromo-derivative, but it is far more stable, and its solution in benzene or chloroform may be boiled for several hours without decomposition. When heated with dilute mineral acids, it is completely hydrolysed into its generators, formaldehyde and 1-chloro-2-naphthylamine.

The decomposition with phloroglucinol was carried out in precisely the same manner as in the case of the analogous bromine compound.

0.4806 gave 0.1687 phloroglucide.  $\text{CH}_2 = 3.51$ .

0.6210 „ 0.2140 „  $\text{CH}_2 = 3.44$ .

$\text{CH}_2(\text{NH} \cdot \text{C}_{10}\text{H}_6\text{Cl})_2$  requires  $\text{CH}_2 = 3.81$  per cent.

The regenerated 1-chloro-2-naphthylamine was precipitated from the filtrates and recrystallised from petroleum; it then melted at  $59^\circ$  (corr.  $60^\circ$ ).

#### *Preparation of Dimethyl- $\beta$ -naphthylamine.*

This base is most conveniently obtained by the method employed by Bamberger (*Ber.*, 1889, 22, 1306). 143 grams of  $\beta$ -naphthylamine (1 mol.), intimately mixed with caustic soda ( $2\frac{1}{2}$  mols.) and 90 c.c. of water, are heated with methyl iodide (3 mols.) at  $120^\circ$  for 5—6 hours. The  $\beta$ -naphthyltrimethylammonium iodide thus produced is separated from the admixed oily impurities by crystallisation from water. It separates in lustrous, white leaflets, the yield obtained from the above quantities being about 210 grams.

A small amount of dimethyl- $\beta$ -naphthylamine is produced by the dry distillation of the quaternary iodide, but the base is obtained in almost quantitative yield by gently heating the corresponding chloride or hydroxide.

The chloride is produced by digesting a warm solution of the iodide with freshly precipitated silver chloride; it is extremely soluble, and can only be isolated in the form of its *platinichloride*. This substance crystallises from alcohol in transparent, orange plates, and melts at  $198^\circ$ .

0.2225 gave 0.559 Pt.  $\text{Pt} = 25.12$ .

$(\text{C}_{10}\text{H}_7\text{NMe}_3)_2\text{PtCl}_6$  requires  $\text{Pt} = 25.00$  per cent.

When the aqueous solution of  $\beta$ -naphthyltrimethylammonium chloride is evaporated to dryness, methyl chloride is evolved and dimethyl- $\beta$ -naphthylamine remains in the residue. The same result is attained by evaporating down a solution of  $\beta$ -naphthyltrimethylammonium hydroxide prepared by digesting the iodide with mois t

silver oxide. In both cases, the reaction is completed by raising the temperature of the residue to 130°. The dimethyl- $\beta$ -naphthylamine solidifies on cooling, and, after two crystallisations from dilute methyl alcohol, melts at 46°.

*Action of Formaldehyde on Dimethyl- $\beta$ -naphthylamine. 2:2'-Tetramethyldiamino-1:1'-dinaphthylmethane.*

Dimethyl- $\beta$ -naphthylamine (10 grams), dissolved in 50 grams of glacial acetic acid and 20 grams of acetic anhydride, is treated with 5 grams of formaldehyde solution (35 per cent.). There is no change in the colour of the solution, nor is there any appreciable rise of temperature, the reaction being far less energetic than in the case of  $\beta$ -naphthylamine. After remaining for 12 hours, the solution is poured into cold water, the excess of acid neutralised with ammonia, and the precipitated base dried on porous plates. The yield is quantitative.

2:2'-Tetramethyldiamino-1:1'-dinaphthylmethane,  $\text{CH}_2[\text{C}_{10}\text{H}_6\cdot\text{N}(\text{CH}_3)_2]_2$ , is readily soluble in methyl or ethyl alcohol or ethyl acetate, and crystallises from these solvents in transparent, colourless, flattened prisms with obliquely truncated ends. It melts at 144°.

0.1317 gave 0.4095  $\text{CO}_2$  and 0.0878  $\text{H}_2\text{O}$ . C = 84.80; H = 7.40.

0.1529 „ 0.4719  $\text{CO}_2$  „ 0.1042  $\text{H}_2\text{O}$ . C = 84.71; H = 7.57.

0.1041 „ 7.4 c.c. moist-nitrogen at 21° and 756 mm. N = 8.04.

$\text{C}_{25}\text{H}_{26}\text{N}_2$  requires C = 84.74. H = 7.34; N = 7.91 per cent.

The *picrate* crystallises from alcohol in yellow leaflets melting at 193—194°.

Unlike dimethyl- $\beta$ -naphthylamine, the new base shows no tendency to form a quaternary iodide; combination does not occur when it is heated for some hours at 110° with excess of methyl iodide.

*Preparation of Diethyl- $\beta$ -naphthylamine.*

Diethyl- $\beta$ -naphthylamine has been studied previously (*Ber.*, 1889, 22, 1761), but no account of its preparation is to be found in the literature. It may, however, be prepared more readily than dimethyl- $\beta$ -naphthylamine, its lower homologue, as the ethylation stops at the formation of the tertiary base.

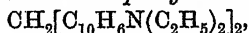
An intimate mixture of 39 grams of  $\beta$ -naphthylamine, 22 grams of caustic soda, and 22 c.c. of water was heated with 85 grams of ethyl iodide (2 mols.) in sealed tubes, at 120°, for 7—8 hours. The product was an oil, which was dried over caustic potash, and subsequently fractionated. The greater portion distilled over between 309° and 313°. This fraction did not give a nitrosamine when treated with hydrochloric acid and sodium nitrite, and was not acted on by acetic

anhydride. It was again fractionated, and the portion boiling at 310—312° (uncorr.) under 764 mm. pressure was utilised in the following experiment.

*Action of Formaldehyde on Diethyl-β-naphthylamine. 2:2'-Tetraethyl-diamino-1:1'-dinaphthylmethane.*

A solution containing 18 grams of diethyl-β-naphthylamine in 30 grams of glacial acetic acid and 8 grams of acetic anhydride was treated with 5 grams of formaldehyde solution (35 per cent.); the mixture, after remaining for 12 hours, was heated to boiling for a few minutes, and then added to a large volume of cold water. The solution was neutralised with ammonia, and the semi-solid mass which separated was collected and drained on porous plates. The yield of crude base was about 16 grams.

2:2'-Tetraethyldiamino-1:1'-dinaphthylmethane,



crystallises from ethyl acetate in large, transparent, colourless, tabular prisms, melts at 114°, and is more soluble than its tetramethyl homologue, which it resembles in appearance. For the purpose of analysis, a portion was crystallised from ethyl alcohol.

0.1436 gave 0.4500 CO<sub>2</sub> and 0.1083 H<sub>2</sub>O. C=85.46; H=8.38.

0.2118 „ 0.6626 CO<sub>2</sub> „ 0.1627 H<sub>2</sub>O. C=85.31; H=8.53.

0.1845 „ 11 c.c. moist nitrogen at 17° and 764 mm. N=6.94.

0.3554 „ 21.7 c.c. „ „ „ 13.5° and 741 mm. N=7.06.

C<sub>29</sub>H<sub>34</sub>N<sub>2</sub> requires C=84.88; H=8.29; N=6.83 per cent.

I was enabled, through the kindness of Dr. Sidney Williamson, to compare the diethyl-β-naphthylamine, prepared by the above method, with a specimen of the base employed in his researches with Bamberger (*Ber.*, 1889, 22, 1761). The latter specimen, when condensed with formaldehyde, yielded a base which crystallised from ethyl acetate in transparent, tabular prisms melting at 114°, and was identical in every respect with the base obtained from my preparation.

*Formaldehyde and ar-Tetrahydrodiethyl-β-naphthylamine.*

Six grams of *ar*-tetrahydrodiethyl-β-naphthylamine (b. p. 296°), dissolved in 48 grams of a mixture of glacial acetic acid and acetic anhydride (1:1), were treated at the ordinary temperature with 3.5 c.c. of formaldehyde solution (35 per cent.). After a fortnight the solution was neutralised with ammonia and extracted with ether; the basic oil obtained proved to be the unaltered substance and 3—4 grams were recovered boiling at 293—297° under 748 mm. pressure,

A similar negative result was obtained on heating the solution of base and aldehyde at 100—110° for several hours.

*Benzylation of  $\beta$ -Naphthylamine. Dibenzy- $\beta$ -naphthylamine.*

A mixture of  $\beta$ -naphthylamine (1 mol.) and benzyl chloride ( $2\frac{1}{2}$  mols.) with a slight excess of 10 per cent. caustic soda solution, was heated at 100° for 7—8 hours, and the tarry product, after washing with warm water until free from alkali, was digested with cold ethyl alcohol to remove any unaltered  $\beta$ -naphthylamine. When a small portion of the alcoholic washings treated with hydrochloric acid and sodium nitrite no longer gave a red coloration with an alkaline solution of  $\beta$ -naphthol, the residue was dissolved in hot ethyl acetate. The solution, on cooling, deposited hard, nodular crystals melting at 118°. After repeated crystallisations from alcohol, in which the base is sparingly soluble, transparent, colourless lath-like crystals were obtained, melting at 119—120°; these became slightly pink on exposure to the air. On analysis:

0.1542 gave 0.5058  $\text{CO}_2$  and 0.0899  $\text{H}_2\text{O}$ . C = 89.39; H = 6.42.

0.1074 „ 4.3 c.c. moist nitrogen at 19° and 763 mm. N = 4.62.

$\text{C}_{24}\text{H}_{21}\text{N}$  requires C = 89.16; H = 6.50; N = 4.30 per cent.

*Dibenzy- $\beta$ -naphthylamine*,  $\text{C}_{10}\text{H}_7\cdot\text{N}(\text{C}_7\text{H}_7)_2$ , crystallises in the free state from glacial acetic acid, and its salts are decomposed by water.

The *picrate* crystallises from an alcoholic solution in opaque, yellow scales, melting at 137—138°.

The *platinichloride* is obtained from an alcoholic solution as a brownish-yellow precipitate.

Monobenzy- $\beta$ -naphthylamine, which has been prepared by reducing benzylidene- $\beta$ -naphthylamine with sodium amalgam in alcoholic solution (*Annalen*, 1887, 241, 260), was not obtained by direct benzylation.

*Action of Formaldehyde on Dibenzy- $\beta$ -naphthylamine. 2:2'-Tetrabenzyldiamino-1:1'-dinaphthylmethane.*

The condensation with formaldehyde takes place less readily with dibenzy- $\beta$ -naphthylamine than with the two dialkyl- $\beta$ -naphthylamines.

A solution of 3.2 grams of dibenzy- $\beta$ -naphthylamine in 40 grams of glacial acetic acid and 3 grams of acetic anhydride was treated with 5 c.c. of formaldehyde solution (35 per cent.), the mixture heated to boiling and then allowed to cool. The first crop of crystals which separated consisted of the unaltered base, and melted at 114°. On allowing the filtrate to remain overnight, a second crop separated; this appeared to be a mixture, for it melted somewhat indefinitely, softening at 140° and fusing at 154°. After recrystallisation from ethyl acetate, the

melting point was raised to  $164^{\circ}$ . As condensation had evidently been effected, the experiment was repeated with a similar mixture, but on boiling for 4—5 hours only tarry products were obtained.

The condensation product was best obtained in the following manner. A solution containing 6 grams of dibenzyl- $\beta$ -naphthylamine in 60 c.c. of glacial acetic acid and 4 grams of acetic anhydride was treated in the cold with 2.5 c.c. of formaldehyde solution, and then gently boiled for 30—45 minutes; on cooling, it deposited a white, crystalline substance which melted at  $159$ — $160^{\circ}$ . 2:2-Tetrabenzyl-diamino-1:1'-dinaphthylmethane,  $\text{CH}_2[\text{C}_{10}\text{H}_6\cdot\text{N}(\text{C}_6\text{H}_5)_2]_2$ , is sparingly soluble in alcohol, and forms transparent, colourless, glistening plates melting at  $164$ — $165^{\circ}$ .

0.1516 gave 0.4977  $\text{CO}_2$  and 0.0883  $\text{H}_2\text{O}$ . C = 89.53; H = 6.40.

$\text{C}_{49}\text{H}_{42}\text{N}_2$  requires C = 89.36; H = 6.38 per cent.

The three dinaphthylmethane derivatives, unlike tetramethyldiaminodiphenylmethane, do not yield coloured substances on treatment with lead peroxide or benzoyl chloride.

*Action of Formaldehyde on Dimethyl- $\alpha$ -naphthylamine. 1:1'-Tetramethyldiaminodinaphthylmethane.*

Dimethyl- $\alpha$ -naphthylamine was prepared according to the method given by Hantzsch (*Ber.*, 1880, 13, 1348; 1888, 21, 3124) and purified from traces of  $\alpha$ -naphthylamine and monomethyl base by treatment with acetic anhydride. The product employed in the following experiments boiled at  $270$ — $271^{\circ}$  under 755 mm. pressure.

A solution of 4 grams of dimethyl- $\alpha$ -naphthylamine in 20 grams of cold glacial acetic acid, treated with 1 c.c. of formaldehyde solution (35 per cent.) and 1 c.c. of concentrated hydrochloric acid, was allowed to remain overnight, then heated to boiling for a few minutes and poured into cold water. The excess of acid was neutralised with ammonia and the pasty mass which separated was drained on porous plates and recrystallised from ethyl acetate.

1:1'-Tetramethyldiaminodinaphthylmethane,  $\text{CH}_2[\text{C}_{10}\text{H}_6\cdot\text{N}(\text{CH}_3)_2]_2$ , separates from ethyl acetate in clusters of hard, transparent, colourless prisms which become tinged with yellow on exposure; it melts at  $177^{\circ}$ .

0.1798 gave 0.5554  $\text{CO}_2$  and 0.1164  $\text{H}_2\text{O}$ . C = 84.28; H = 7.19.

0.1499 „ 0.4650  $\text{CO}_2$  „ 0.1007  $\text{H}_2\text{O}$ . C = 84.60; H = 7.47.

0.0865 „ 5.8 c.c. moist nitrogen at  $14.5^{\circ}$  and 768 mm. N = 7.95.

$\text{C}_{26}\text{H}_{26}\text{N}_2$  requires C = 84.74. H = 7.34; N = 7.91 per cent.

Since there is a possibility of obtaining three isomerides in this condensation, the mother liquors from the compound melting at  $177^{\circ}$



were allowed to evaporate nearly to dryness. It was found, however, that the crystals which had separated melted at  $172^{\circ}$  and gave the same melting point when mixed with an equal amount of the substance from the first crop.

1:1'-Tetramethyldiaminodinaphthylmethane is not oxidised to a coloured substance by lead peroxide; in this respect it resembles the compound obtained by Friedländer and Welms from dimethyl- $\alpha$ -naphthylamine and benzaldehyde (*Ber.*, 1888, 21, 3123).

*Action of Formaldehyde on Ethyl- $\beta$ -naphthylamine. 2:2'-Diethyldiamino-1:1'-dinaphthylmethane.*

Ethyl- $\beta$ -naphthylamine was prepared according to the method described by Otto Fischer (*Ber.*, 1893, 26, 193), and the product employed in the following experiments, boiled at  $309\text{--}311^{\circ}$  under 758 mm. pressure. The freshly distilled base is almost colourless, but rapidly darkens on exposure to light, and develops an intense blue fluorescence.

2:2'-Diethyldiamino-1:1'-dinaphthylamine,  $\text{CH}_2(\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{C}_2\text{H}_5)_2$ .—To prepare this base, 7 grams of formaldehyde solution are added to a solution of 20 grams of ethyl- $\beta$ -naphthylamine in 80 grams of glacial acetic acid. The solution assumes a deep colour, and rapidly becomes pasty from the separation of a crystalline precipitate; the reaction is accompanied by an appreciable rise in temperature, but cooling with ice is not necessary. The precipitate is washed with acetic acid and alcohol until colourless; the filtrate is added to a large volume of water, the acid neutralised with ammonia, and the yellow, viscid mass which separates extracted with chloroform; the extract yields a further quantity of the condensation product. The precipitate and the substance extracted with chloroform are mixed together, and crystallised from ethyl acetate, from which the base separates in well defined, transparent, colourless plates, melting at  $197\text{--}198^{\circ}$ . The following numbers were obtained on analysis:

0.1124 gave 0.3475  $\text{CO}_2$  and 0.0761  $\text{H}_2\text{O}$ . C = 84.31; H = 7.52.  
 0.1450 „ 0.4500  $\text{CO}_2$  „ 0.0960  $\text{H}_2\text{O}$ . C = 84.64; H = 7.35.  
 0.1685 „ 11.6 c.c. moist nitrogen at  $20^{\circ}$  and 765 mm. N = 7.82.  
 $\text{C}_{25}\text{H}_{26}\text{N}_2$  requires C = 84.74; H = 7.34; N = 7.91 per cent.

The experiment was repeated with a large excess of formaldehyde in order to see whether further condensation in the side chains would occur, but 2:2'-diethyldiamino-1:1'-dinaphthylmethane was the only product. This base is also produced by dissolving ethyl- $\beta$ -naphthylamine hydrochloride in glacial acetic acid, and adding successively the requisite quantities of sodium acetate and formaldehyde solution.

The *dibenzoyl* derivative,  $\text{CH}_2[\text{C}_{10}\text{H}_6\cdot\text{N}(\text{C}_2\text{H}_5)\cdot\text{CO}\cdot\text{C}_6\text{H}_5]_2$ , was prepared by the Schotten-Baumann method. The semi-solid mass, obtained by shaking up the base with excess of benzoyl chloride and a solution of caustic potash, was triturated with ether to remove an oily impurity, and the crystalline solid, after drying on porous plates, extracted with benzene. To the filtered solution, an equal volume of petroleum was added, and the benzoyl derivative, obtained in small, colourless plates, was recrystallised from alcohol. It forms transparent, colourless, highly refractive prisms, and melts at  $196^\circ$ . This melting point is very close to that of the original base, but a mixture of the two substances melts at  $171\text{--}172^\circ$ .

0.1650 gave 7.1 c.c. moist nitrogen at  $18^\circ$  and 764 mm.  $\text{N} = 4.99$ .

$\text{C}_{39}\text{H}_{34}\text{O}_2\text{N}_2$  requires  $\text{N} = 4.97$  per cent.

*Action of Formaldehyde on Ethyl- $\beta$ -naphthylamine Hydrochloride in Alcoholic Solution.*

Twenty-five grams of ethyl- $\beta$ -naphthylamine hydrochloride dissolved in 300 grams of alcohol were heated for 15 minutes with 13 grams of formaldehyde solution. The colour of the solution changed from light brown to deep red, and a precipitate was produced. The alcohol was removed as far as possible by distillation, the residue washed with water, filtered, boiled with alcoholic potash, poured into water, and the precipitated bases collected, dried on porous plates, and extracted with benzene. The benzene extract, on cooling, yielded a dark brown, crystalline precipitate, which was again crystallised from this solvent. The product was a mixture of two bases, and their complete separation was a matter of some difficulty. The mixture was dissolved in ethyl acetate, and the first crop of crystals repeatedly crystallised from this solvent until the melting point remained constant. The substance separated in colourless plates melting at  $197\text{--}198^\circ$ , and was identified as 2:2-diethyldiamino-1:1'-dinaphthylmethane, the base obtained in the preceding condensation.

The ethyl acetate mother liquors, on the addition of alcohol, gave a light brown, crystalline precipitate, which was crystallised from alcohol until the melting point remained constant at  $157\text{--}158^\circ$ . The substance separates in transparent, colourless prisms, which become opaque on warming, and darken on exposure to light. A portion, dried at  $90\text{--}100^\circ$  until constant in weight, was analysed, with the following results:

0.2547 gave 0.7915  $\text{CO}_2$  and 0.1441  $\text{H}_2\text{O}$ .  $\text{C} = 84.70$ ;  $\text{H} = 6.37$ .

0.1511 " 0.4703  $\text{CO}_2$  " 0.0882  $\text{H}_2\text{O}$ .  $\text{C} = 84.88$ ;  $\text{H} = 6.40$ .

0.1710 " 6.3 c.c. moist nitrogen at  $19^\circ$  and 770 mm.  $\text{N} = 4.29$ .

Another specimen, crystallised from benzene, remained constant in weight when heated for  $1\frac{1}{2}$  hours at  $90-100^\circ$ , and was analysed.

0.1739 gave 0.5401  $\text{CO}_2$  and 0.1028  $\text{H}_2\text{O}$ .  $\text{C}=84.70$ ;  $\text{H}=6.56$ .

0.1969 „ 0.6085  $\text{CO}_2$  „ 0.1147  $\text{H}_2\text{O}$ .  $\text{C}=84.28$ ;  $\text{H}=6.47$ .

0.2558 „ 9.6 c.c. moist nitrogen at  $16^\circ$  and 772 mm.  $\text{N}=4.44$ .

$\text{C}_{23}\text{H}_{19}\text{ON}$  requires  $\text{C}=84.92$ ;  $\text{H}=5.84$ ;  $\text{N}=4.30$  per cent.

The analytical results indicate that the substance contains oxygen, and that it is formed by the elimination of half the nitrogen from two mols. of ethyl- $\beta$ -naphthylamine (see p. 819).

It is very soluble in ethyl acetate or chloroform, and crystallises from its solution in either solvent in well defined, colourless prisms. When crystallised from alcohol and dried at the ordinary temperature, it contains 1 mol. of alcohol of crystallisation. An air-dried specimen gave the following numbers:

0.1403 gave 0.4154  $\text{CO}_2$  and 0.0910  $\text{H}_2\text{O}$ .  $\text{C}=80.74$ ;  $\text{H}=7.20$ .

$\text{C}_{23}\text{H}_{19}\text{ON} + \text{C}_2\text{H}_6\text{O}$  requires  $\text{C}=80.86$ ;  $\text{H}=7.01$  per cent.

The base,  $\text{C}_{23}\text{H}_{19}\text{ON}$ , when treated with acetic anhydride, benzoyl chloride (Schotten-Baumann method), or hydriodic acid and red phosphorus at  $170^\circ$  gives rise to resinous products.

The formation of a compound having the above constitution involves the elimination of ethylamine, and this base was identified in the following manner. The aqueous filtrate from the original precipitate was rendered alkaline, and distilled in a flask fitted with Kjeldahl bulbs, the ammoniacal gas evolved being passed into hydrochloric acid. On the addition of platinic chloride, an orange platinichloride was obtained which crystallised in hexagonal plates. On analysis:

0.3403 gave 0.1322 Pt.  $\text{Pt}=38.84$ .

0.3926 „ 0.1522 Pt.  $\text{Pt}=38.80$ .

$(\text{C}_2\text{H}_5\cdot\text{NH}_2)_2\text{H}_2\text{PtCl}_6$  requires  $\text{Pt}=39.00$  per cent.

Considerable progress has been made in the study of the action of benzaldehyde and its analogues on the alkyl and halogen derivatives of  $\beta$ -naphthylamine, and the results will be made known in a subsequent communication.

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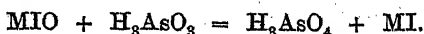
# LXXV.—*Estimation of Hypiodites and Iodates and the Reaction of Iodine Monochloride with Alkalis.*

By K. J. P. ORTON and W. L. BLACKMAN.

SEVERAL characteristic properties of solutions of hypiodites have been recorded, that is, of solutions obtained by causing iodine (in the solid form or in solution) to react with solutions of alkalis.

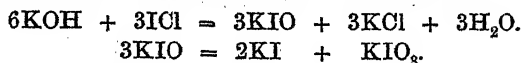
The evolution of oxygen from hydrogen peroxide and barium peroxide, and the liberation of iodine from potassium iodide were noted by Schönbein (*J. pr. Chem.*, 1861, 84, 385) and Seliwanow (*Ber.*, 1894, 27, 1013); and the bleaching of indigo carmine and cochineal by Lunge and Schock (*Ber.*, 1882, 15, 1883). The former reaction they attempted to apply quantitatively. Lonnes (*Zeit. anal. Chem.*, 1894, 33, 409) found that sodium arsenite, and Péchard (*Compt. rend.*, 1899, 128, 1453) that ferrous sulphate, were oxidised by these solutions.

The authors have used a modification of a method, proposed by Lonnes (*loc. cit.*), in which the oxidation of arsenite is employed to estimate the hypiodite, the reaction being represented by the following equation:



The iodate is estimated by acidifying the solution and titrating the iodine liberated by sodium sulphite or thiosulphate.

The solutions were prepared by mixing solutions of iodine in potassium iodide with alkalis, and from solutions of iodine monochloride in hydrochloric acid\* and alkalis. The reaction of iodine monochloride with alkalis is shown to be represented by the equation.



Initially, no potassium iodide is formed as in the reaction of iodine and alkalis. As the presence of potassium iodide has a disturbing effect, a greater excess of alkali is necessary before the reaction of iodine with starch or chloroform ceases (compare Lonnes and Péchard, *loc. cit.*). In our experiments, sufficient alkali was always present to ensure the absence of any free iodine. The solutions prepared resemble those obtained from iodine; they have a characteristic odour

\* A 3/10 to 4/10 *N* solution of iodine monochloride is easily made by gently warming 10 grams of iodine with a mixture of the calculated quantity (2.8 c.c.) of nitric acid of sp. gr. 1.4, and 30–40 c.c. of concentrated HCl of sp. gr. 1.15. When all the iodine has dissolved, the solution is diluted to 250 c.c. with water or dilute hydrochloric acid.

resembling that of iodoform or saffranine, and are pale straw-yellow. They oxidise arsenite, sulphite, and thiosulphate immediately. On standing, the hypiodite disappears, and in most cases is not recognisable after 24 hours; ammonium hypiodite, however, is much more stable and is not wholly decomposed after 2 weeks. When not too dilute, they give a precipitate of nitrogen iodide with ammonia. A trace of hypiodite is readily recognisable, when no large quantity of alkali is present, by adding first sodium or potassium hydrogen carbonate and starch and finally potassium iodide. A blue colour immediately appears. If iodide is already present in quantity, the blue colour develops without the addition of potassium iodide (compare Taylor, this vol., 729).

*Estimation of Hypiodites and Iodate.*

Excess of a standard solution of sodium arsenite is added to the alkaline hypiodite. After standing for a short time, the alkali is removed by carbon dioxide,\* and then the excess of arsenite estimated by standard iodine. Experiments have shown that under these circumstances the arsenite is not affected by iodate and iodide (compare Lonnes, *loc. cit.*). When ammonia is the alkali, it can be removed partly by boiling. The iodate is now estimated by adding a little dilute sulphuric acid, and titrating any iodine set free. A further quantity of sulphuric acid is added, and followed by addition of sulphite (or thiosulphate), and so on, until the solution is acid. This procedure avoids loss of iodine by the evolution of carbon dioxide, and further prevents the solution from ever becoming very acid, with the consequent interaction of the arsenate with the hydriodic acid. The following experiments show that this method is fairly trustworthy.

(1) To 100 c.c. of a solution containing 0.59 gram of potassium iodate and about 1 gram of potassium iodide, 10 c.c. of a 35 per cent. solution of potassium hydroxide were added, and then 26.6 c.c. of *N*/10 arsenious oxide. The solution was now saturated with carbon dioxide and allowed to stand 4 days. 26.6 c.c. *N*/10 iodine were required to oxidise the arsenite. The iodate was now estimated in an aliquot part. 0.5904 gram was found.

(2) 7.15 c.c. of *N*/10 arsenious oxide were added to a solution of ammonia (3*N*) containing 0.1 gram of potassium iodate. After partial removal of the ammonia by boiling and conversion into carbonate by carbon dioxide, 7.15 c.c. *N*/10 iodine were required to oxidise the arsenite, and 0.1003 gram of potassium iodate was found.

Similar experiments gave equally satisfactory results. As a rule, the amount of iodate found is slightly in excess of that taken.

\* Lonnes only used such dilute solutions of alkalis that this operation was not necessary.

*Solutions of Potassium and Sodium Hydroxide.*

To a 4 per cent. solution of potash, the solution of iodine monochloride in hydrochloric acid was cautiously added. At intervals, 100 c.c. of hypoiodite solution were withdrawn and titrated as above. The temperature during the experiment was not absolutely constant, but about 15°.

Estimated by distillation with ferric alum and sulphuric acid after conversion of the iodate into iodide by sulphurous acid, the total iodine per 100 c.c. = 24.05 c.c. of *N*/10 iodine, or 0.3054 gram.

Time.	Percentage of iodine as hypoiodite.	Percentage of iodine as iodate and iodide.
5 mins. ....	78.96	21.4
45 „ ....	35.5	64.2
60 „ ....	26.0	73.8
24 hours .....	0.24	100.0

In a similar experiment in which 20 c.c. of *N*/10 iodine in a solution of potassium iodide was added to 100 c.c. of 4 per cent. potassium hydroxide, 77 per cent. of the iodine was present as hypoiodite after 5 minutes, 31 per cent. after 20 minutes, 21.2 per cent. after 30 minutes, and 14 per cent. after 45 minutes.

Many series of analyses similar to the above were made, both with caustic potash and soda, giving the same results. After 24 hours, the whole of the hypoiodite had practically disappeared at the temperature of the laboratory (about 15°). Light had little effect on the rate of transformation. Two exactly similar solutions were made up together—one kept in darkness and the other in diffused daylight. Each was titrated every half-hour. After 1½ hours, 50 c.c. of one oxidised 3.86 c.c., and of the other 3.75 c.c. of *N*/10 arsenious oxide.

With solutions of potash less concentrated than 3 per cent., the whole of the iodine can be found as hypoiodite for a very short time, but with more concentrated solutions some conversion into iodate and iodide had always taken place before the arsenite was added. Thus 5 c.c. of an iodine monochloride solution were added to 75 c.c. of 3 per cent. aqueous potassium hydroxide, and excess of *N*/10 arsenious oxide immediately run in, but only 98.4 per cent. of the iodine was present as hypoiodite.

*Solutions of Calcium and Barium Hydroxide.*

The solutions were made up by adding the acid solution of iodine monochloride to saturated solutions of the alkalis, and also, according to Lunge and Schock's directions, by grinding up iodine with calcium

hydroxide and water, filtering, and making up to a given volume. The solutions obtained by each of these methods were titrated with arsenite and standard indigo. In the latter case, after addition of the indigo, the solution was allowed to stand for 15 minutes, and then the excess titrated with bleaching powder.

(1) *N*/25 calcium hydroxide solution. Temperature about 15°. Total iodine per 100 c.c. = 1.92 c.c. of *N*/10 iodine, or 0.0244 gram.

Time.	Percentage of iodine as hypoiodite.	Percentage of iodine as iodate and iodide.	c.c. of <i>N</i> /10 indigo bleached.
5 mins. ....	95.6	3.1	7.4
45 „ ....	68.7	29.6	7.0
17 hours .....	8.4	91.1	6.0

(2) A solution made by Lunge and Schook's method, and containing iodine = 5.65 c.c. of *N*/10 iodine per 100 c.c. (= 0.0717 gram) after standing for 70 hours, did not oxidise arsenite, but bleached indigo. In two titrations, 100 c.c. bleached (a) 5.4 c.c., (b) 5.8 c.c. of *N*/10 indigo.

When iodine in potassium iodide is used, similar results are obtained. With iodine monochloride all the iodine has been found present as hypoiodite for a short time.

The transformation into iodate and iodide is considerably slower than with potassium hypoiodite. Thus, in 45 minutes, at about 15°, only 35 per cent. of hypoiodite has disappeared; while with potassium hypoiodite considerably more than 60 per cent. has disappeared in the same time. The indigo, bleached by a given solution, is seen to bear no relation to the arsenite oxidised, or, indeed, to the iodine present. The action on indigo decreases but little as the hypoiodite diminishes, and is considerable with solutions which do not act on arsenite. This action is due to the alkali alone. Thus, after adding indigo to 100 c.c. of calcium hydroxide solution, and estimating the former after 15 minutes standing, 5.3 c.c. of *N*/10 indigo had disappeared. The bleaching effect observed by Lunge and Schook in their solutions, which had stood for 24 hours, is therefore probably due to the alkali, and not to hypoiodite (compare Taylor, *Trans.*, 1900, 77, 729).

#### *Solutions of Ammonia and Methylamine.*

In the case of ammonia, only dilute solutions could be obtained, owing to the precipitation of nitrogen iodide on further addition of iodine monochloride. Admixture of iodine monochloride and methylamine solution (3*N*) produces a yellow solution, and only after a considerable quantity of iodine monochloride has been added does a precipitate of methylthiodoamine,  $\text{CH}_3\cdot\text{NI}_2$ , appear. The alkaline

solutions thus obtained in many ways resemble hypiodite solutions in their behaviour towards arsenite, and towards potassium iodide and sodium hydrogen carbonate, only they are far more stable. With ammonia, the formation of iodate and iodide is very slow, the change not being complete at the end of two weeks. With methylamine, the power of oxidising arsenite slowly diminishes, but in three weeks has not entirely disappeared. Iodate is only formed in very small quantity, and cannot be detected for the first few days. Iodide is produced in the solution from the product formed initially.

(1) 3*N* aqueous ammonia. Temperature 12–14°.

Total iodine per 100 c.c. = 0.9 c.c. of *N*/10 iodine = (0.0114 gram).

Time.	Per cent. of iodine as hypiodite.	Per cent. of iodine as iodate and iodide.
15 mins.....	99.5	0.0
24 hours.....	83.3	13.3
48 „ .....	77.7	22.2
72 „ .....	66.6	35.5
28 days .....	8.8	93.3

These titrations were carried out with 300 c.c. of the solution, using *N*/100 standard solutions.

(2) 3*N* methylamine solution. Temperature 15°.

Total iodine per 100 c.c. = 20.4 c.c. of *N*/10 iodine (= 0.259 gram).

Time.	Per cent. of iodine as hypiodite.	Per cent. of iodine as iodate and iodide.
15 mins.....	100.2	0.0
1 hour .....	99.2	0.0
19 hours.....	86.7	0.0
48 „ .....	74.8	0.0
24 days .....	7.1	2.7

It was thought that possibly in the case of methylamine the arsenite was oxidised by iodate, but this was shown not to be the case by a blank experiment. Also the same amount of oxidation of arsenite took place when excess of concentrated sodium hydroxide was added to the methylamine solution before the arsenite was run in. It appears then that the initially formed product, whether methyldiiodoamine,  $\text{CH}_3\cdot\text{NI}_2$ , or hypiodite, is fairly stable, and is only slowly converted into hydriodic acid (methylamine hydriodide) probably in oxidising some of the methylamine. This point will be further investigated.



*Reaction of Iodine with Mercuric Oxide.*

Köne (*Poggendorff's Annalen*, 1845, 66, 302) and Lippmann (*Compt. rend.*, 1866, 63, 968) have noticed the formation of hypiodous acid (or mercury hypiodite) when iodine is shaken up with water and mercuric oxide. In the presence of amylene, Lippmann observed the formation of an iodohydrin. We have estimated the amount of hypiodite and iodate in solutions prepared by shaking up finely-powdered iodine and mercuric oxide (precipitated) with water, alcohol being omitted owing to the action of hypiodite on it. The shaking was continued for a few minutes, and the solution then filtered through asbestos or hardened filter paper. The solutions were neutral or faintly acid, the latter being the case when the shaking was not prolonged. They were colourless and gave no reaction with starch paste on acidifying or on adding sodium hydrogen carbonate. For some hours (3—4), they gave the reaction for hypiodite with sodium hydrogen carbonate, starch paste, and potassium iodide. On addition of potassium iodide to the acidified solution, it became deep brown from the liberation of iodine, a reaction which points to the presence of iodate.

A solution prepared by shaking iodine with mercuric oxide for 5 minutes contained iodine per 100 c.c. = 2.3 c.c. of *N*/10 iodine, of which 48 per cent. was present as hypiodite, and the remainder as iodate.

In a similar experiment, after 15 minutes shaking, 4.4 c.c. of *N*/10 iodine were contained in 100 c.c., 13—14 per cent. of which was in the form of hypiodite. The filtering of the solution, &c., occupied some 10 minutes after the cessation of the shaking.

From these results, it would seem that the solutions obtained from iodine and mercuric oxide contain only a small quantity of hypiodite, and that the iodine is chiefly present as iodate. Iodide is only present in small quantity, owing to the low solubility of mercuric iodide.

No attempt was made to determine the velocity constant of these transformations of hypiodite. Schwicker (*Zeit. physikal. Chem.*, 1895, 16, 303) has attempted to determine this constant for the transformation of potassium hypiodite, and found that it varied greatly with the variations in initial concentration of the hypiodite and the alkali. Excess of potassium iodide was present in the solutions. It is possible that the investigations of the solutions of calcium hypiodite or ammonium hypiodite (?) which undergoes transformation relatively slowly may lead to some elucidation of this point.

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LXXVI.—*Researches on Silicon Compounds. Part VI.  
On Silicodiphenyldiimide and Silicotriphenylguanidine.*

By J. EMERSON REYNOLDS, D.Sc., M.D., F.R.S.

IN Part V of this series of papers (Trans., 1889, 55, 474), I described the well defined, crystalline silicophenylamide,  $\text{Si}(\text{NH}\cdot\text{C}_6\text{H}_5)_4$ , which proved to be the first of a new class of compounds in which silicon is exclusively united with nitrogen. In the course of the paper on the phenylamide, I pointed out that when the crystals were heated somewhat beyond their melting point,  $137^\circ$ , they easily lost some aniline, and added that "the residue consisted of a mixture of silicon compounds to be described later on." The nature of each of these products was, in fact, afterwards made known in the course of my Presidential Address to Section B of the British Association at Nottingham, but no details were then given, and I now desire to repair that omission preliminary to laying before the Society an account of more recent investigations.

The primary interest which attaches to the examination of the changes effected by heating the silicophenylamide is due to the probable production of silicon analogues of cyanogen compounds.

In the preliminary experiments, it was observed that about one-fourth of the total nitrogen of the anilide was easily driven off by heat in the form of aniline, and that a rather higher temperature was necessary for the removal of another fourth. At the end of this second stage, the previously fluid mass suddenly solidified, but continued heating of this residue led to the expulsion of more aniline. Of the three stages of decomposition recognised, that of solidification was most strongly marked, and therefore was first examined in detail.

Twelve grams of silicophenylamide,  $\text{Si}(\text{NH}\cdot\text{C}_6\text{H}_5)_4$ , were heated in a platinum boat placed in a glass tube through which a current of carefully dried hydrogen slowly passed. The gas carried with it the aniline evolved on decomposition, and the latter was condensed in a U-tube, whence it fell into a small measuring vessel. The process was stopped when the aniline collected represented half the nitrogen present in the weight of the anilide taken, and this point was found to coincide with that of the solidification of the residue already mentioned. The aniline collected contained a small quantity of a silicon compound, carried over in the current of gas and vapour.

The residue when cold was broken up and digested with carefully dried benzene, which dissolved little of the material, but removed adherent aniline, unchanged anilide, and another substance. When

purified by this treatment, the product was a white, amorphous powder, quite insoluble in benzene, light petroleum, carbon disulphide, ether, or alcohol. When heated with alcoholic solution of sodium or potassium hydroxide, it gradually dissolved with separation of aniline and evolution of a slight odour of phenyl isocyanide.

0.2912 gave 0.0816  $\text{SiO}_2$ .  $\text{Si} = 13.12$ .

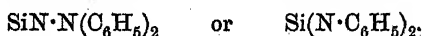
0.351 „ 0.0993  $\text{SiO}_2$ .  $\text{Si} = 13.2$ .

0.263 „ 30.8 c.c. moist nitrogen at  $15^\circ$  and 767 mm.  $\text{N} = 13.76$ .

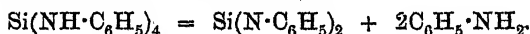
$\text{SiN}_2(\text{C}_6\text{H}_5)_2$  requires  $\text{Si} = 13.33$ ;  $\text{N} = 13.33$  per cent.

The nitrogen is rather high, but this was subsequently explained by the presence of traces of another compound richer in nitrogen, which is formed at an earlier stage of the decomposition, but was unknown at the time the analyses were made, and was not completely removed by benzene.

The new substance may obviously be regarded as the silicon analogue, either of diphenylecyanamide or of carbodiphenyldiimide.

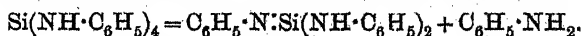


The genesis of the compound from monophenylic groups and the separation of aniline, rather than diphenylamine and ammonia, on decomposition by alkalis, lead to the conclusion that it is silicodiphenyldiimide. Hence the action of heat under the conditions stated is essentially represented by the equations :



Another experiment, in which the heating of the phenylamide was stopped just short of the solidification point, gave a residue which was partially soluble in benzene. The latter solution, when evaporated, left a residue similar in appearance to the diimide and, like it, contained 13.1 per cent. of silicon, but it could not be again dissolved in benzene. Hence, an unstable soluble modification of the diimide appears to exist which easily changes into the compound which is insoluble in benzene.

As the heated amide more easily lost the first molecule of aniline than the second, it seemed probable that the following change could be realised and silicotriphenylguanidine or an isomeride be obtained.



Eight grams of the pure silicophenylamide were carefully heated as before in a current of dry hydrogen. When rather more than one molecular proportion of aniline had been collected, the decomposition was stopped, and the residue allowed to cool in hydrogen. There was no thickening of the residue while hot, but it solidified to a yellowish, transparent mass on cooling.

The product was broken up and heated with benzene. This left a small portion undissolved which possessed the characters of the diimide. The benzene solution, when mixed with twice its volume of light petroleum, gave a somewhat crystalline precipitate totally unlike the anilide obtained under similar conditions. This substance was washed with light petroleum to remove any free aniline, again dissolved in benzene, and four volumes of light petroleum were then gradually added. A precipitate formed, which was seen under the microscope to consist chiefly of droplets of a somewhat sticky substance. On standing for some hours, the liquid afforded a number of small crystals, which separated on the sides of the flask in which the precipitation was effected. These crystals were mechanically removed and purified by dissolution in benzene and subsequent separation on addition of light petroleum. This treatment involved much loss owing to the very sensible solubility of the compound in light petroleum.

The purified crystals were short prisms quite distinct in appearance from the original silicophenylamide, and much less completely precipitated from their benzene solution by addition of light petroleum. It did not afford any definite compound with acids, but was decomposed to some extent even by dry hydrogen chloride, as well as by ordinary solvents.

The crystals melted at  $230^{\circ}$ , and commenced to decompose at a slightly higher temperature; the residue did not solidify until cooled to  $131^{\circ}$ .

On analysis, the purest crystals gave Si = 9.11 and N = 14.03 per cent.

$\text{C}_6\text{H}_5 \cdot \text{N} : \text{Si}(\text{NH} \cdot \text{C}_6\text{H}_5)_2$  requires Si = 9.24; N = 13.86 per cent.

The substance is therefore a silicon analogue of a triphenylguanidine in nearly pure condition.

Hence the carefully regulated decomposition of the silicophenylamide by heat leads to the formation of

Silicotriphenylguanidine ...  $\text{C}_6\text{H}_5 \cdot \text{N} : \text{Si}(\text{NH} \cdot \text{C}_6\text{H}_5)_2$  and  
 Silicodiphenyldiimide .....  $\text{Si}(\text{N} \cdot \text{C}_6\text{H}_5)_2$ .

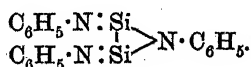
When the action of heat was studied under diminished pressure, at 16 mm., the guanidine stage was quickly passed, and the second molecular proportion of aniline carried over with it a thick liquid of high boiling point, before the residue suddenly changed to the solid diimide. This liquid was easily freed from aniline by careful heating at the low pressure maintained, and when cold was still a viscid substance. This proved to be soluble in benzene, but was precipitated in oily droplets by light petroleum, and adhered to the sides of the vessel in which the substance was thrown down. These droplets solidified after some hours, and then no longer dissolved in benzene.

The viscid liquid so obtained was the unstable form of the diimide already mentioned.

The instability of this viscid liquid suggested the possibility of its being the silicocyanamide, but its action with alkalis was that of the diimide. It is more probable that the unstable liquid represents the simple molecule of the diimide, and that the insoluble and more stable modification is a polymeric form.

When the stable form of the diimide was heated in hydrogen just short of low redness until the evolution of volatile matter ceased, a yellowish, semifused solid was obtained which did not show any charring, but this product was unable to resist a higher temperature.

This residue approximated in composition to that required by the formula



It afforded 17.54 per cent. of Si, and  $\text{Si}_2(\text{N}\cdot\text{C}_6\text{H}_5)_3$  requires Si = 17.1 per cent.

It seemed probable that continued heating in presence of dry ammonia gas would facilitate the removal of the phenyl groups, and this seems to have been the case to some extent, as a residue was obtained by this treatment which was quite white, and contained Si =

32 per cent. The compound,  $\begin{array}{c} \text{HN}:\text{Si} \\ | \\ \text{HN}:\text{Si} \end{array} > \text{N}\cdot\text{C}_6\text{H}_5$ , requires Si = 31.7 per cent.

It was hoped that prolonged heating at a still higher temperature would remove the last phenyl group; but more or less charring occurred, hence the above represents the limit of definite change which has yet been reached by the action of heat alone on the primary substance.

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## LXXVII.—*A Study of the Absorption Spectra of o-Oxy-carbanil and its Alkyl Derivatives in relation to Tautomerism.*

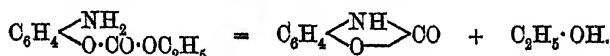
By WALTER NOEL HARTLEY, F.R.S., JAMES J. DOBBIE, D.Sc., M.A.,  
and PHOTIOS G. PALIATSEAS.

THE substance *o*-oxycarbanil,  $\text{C}_7\text{H}_5\text{O}_2\text{N}$ , and its alkyl derivatives form a group of compounds which stand in the same relation to one another as isatin, carbostyryl, and their respective alkyl derivatives.

*o*-Oxycarbanil can be prepared by the fusion of *o*-aminophenol hydrochloride with urea, or from its lactim ether by the action of concentrated hydrochloric acid (Sandmeyer, *Ber.*, 1886, 19, 2650). It can also be obtained by the distillation of *o*-aminophenyl ethyl carbonate (Bender, *Ber.*, 1886, 19, 2269). Two ethyl derivatives of *o*-oxycarbanil are known. One of these is prepared by boiling *o*-oxycarbanil for some time under a reflux condenser with equivalent quantities of ethyl iodide and alcoholic potash, the other by the interaction of *o*-aminophenol and ethyl iminocarbonate. The ether obtained by the first method is considered to be a lactam, that is, to have the ethyl group directly attached to the nitrogen atom, because on heating for some time with hydrochloric acid it takes up water and decomposes into carbon dioxide and the hydrochloride of ethyl *o*-aminophenol.

Its structural formula is therefore  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}(\text{C}_2\text{H}_5) \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CO}$  (Bender, *loc. cit.*). The ether prepared by the second method, on treatment with concentrated hydrochloric acid, yields *o*-oxycarbanil. It is therefore a lactim of the constitution  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{OC}_2\text{H}_5$ .

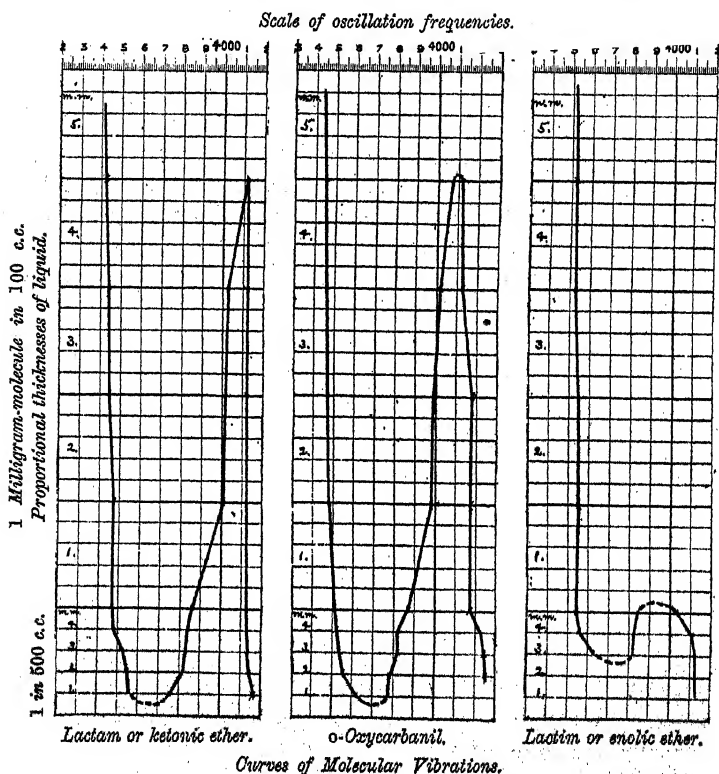
As in the similar cases of isatin and carbostyryl, the chemical evidence leaves the question of the constitution of *o*-oxycarbanil itself undecided. On the one hand, its formation by the distillation of *o*-aminophenyl ethyl carbonate is most easily explained on the assumption that it has the ketonic or lactam constitution, and that the reaction takes place according to the equation :



This view is supported by the fact that it forms a well defined compound with phenylhydrazine (Bender, *loc. cit.*). On the other hand, its direct formation from the lactim ether by the action of hydrochloric acid seems to point to the enolic or lactim structure as being the more probable. It is, however, now generally admitted that arguments based on chemical reactions are inconclusive in cases such as that under consideration, where shifting of a hydrogen atom may easily take place.

The present investigation was undertaken with the view of ascertaining whether a comparison of the absorption spectra of the two ethers, with the absorption spectra of *o*-oxycarbanil, would as in the cases of isatin and carbostyryl (Hartley and Dobbie, *Trans.*, 1899, 75, 640) yield results from which the constitution of the parent substance might be inferred. Assuming that one or other of the ethers differs from *o*-oxycarbanil only in the substitution of the alkyl group for an atom of hydrogen, the constitution of the two substances being other-

wise identical, we should expect the absorption spectra of the parent substance and this ether to be practically the same. On the other hand, the ether which differs in constitution from the parent substance should give a different spectrum. Groenvik (*Bull. Soc. Chim.*, 1876, [ii], 25, 177) gives 136—138°, Sandmeyer 137°, and Bender 141° as the melting point of *o*-oxycarbanil. Although, apart from this slight difference, there was no reason to doubt the identity of the substances obtained by these chemists, we thought it well to examine specimens



prepared independently by two different methods and selected for the purpose, the substances obtained by fusion of *o*-aminophenol with urea and by the decomposition of the lactim ether with hydrochloric acid. We found that the two specimens when heated side by side in capillary tubes behaved in exactly the same way, softening at 137° and melting completely at 139.5°. Solutions of the two specimens gave identical spectra.

The spectra of *o*-oxycarbanil and of the lactam ether are almost

identical. The amount of general absorption is practically the same in both, and the spectra of both substances show a well marked absorption band occupying the same position and persisting, in both cases, through the same range of dilution. The spectra of the enolic ether, on the other hand, show a smaller amount of general absorption, and the absorption band does not appear until a much greater degree of dilution is reached than is required to bring out the band in the other two substances. The range of the band of the enolic ester is also very small. The curves on page 841, drawn from the photographs, show very clearly the relations between the spectra of the various substances.

The conclusion to which the investigation leads is that *o*-oxycarbanil has the same structure as the lactam or ketonic ether, or at all events, that the lactam structure very greatly predominates, if the assumption is made that the parent substance in solution is a mixture of two tautomeric forms. It is worthy of note that in the three cases of this kind which have now been examined, the parent substance possesses the ketonic or lactam constitution.\*

The substances used in this investigation were prepared exactly in accordance with the directions given in the papers already quoted. Two distinct preparations of each substance were made and several series of photographs were taken of the absorption spectra of each preparation. No appreciable difference could be detected in the various photographs of the same substance. This is evidence of the identity of the compounds, and also of the purity of these particular preparations. For an account of the method used in drawing the accompanying curves, the reader is referred to the paper on the absorption spectra of isatin, carbostyryl, &c., already quoted, and to the publications therein named.

#### MEASUREMENTS.

*o*-Oxycarbanil,  $C_7H_6O_2N$ .

0.135 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to ..... Complete absorption beyond.	3382	2956
20	Spectrum continuous to ..... Complete absorption beyond.	3410	2932
15	The same.		

\* *o*-Oxycarbanil, it may be noted, gives no colour reaction with ferric chloride.



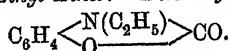
0.135 gram (1 milligram-mol.) in 100 c.c. alcohol (*continued*).

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
10	Spectrum continuous to ..... Complete absorption beyond.	3422	2922
5	Spectrum continuous to ..... <b>Absorption band</b> ..... Strong lines feebly transmitted at .... Complete absorption beyond.	3450 3450 to 4080 4102 and 4122	2898 2898 to 2450 2437 and 2426
4	Spectrum continuous to ..... <b>Absorption band</b> ..... Lines very feebly transmitted at .. ... More strongly at ..... Complete absorption beyond.	3462 3462 to 4029 4029 and 4080 4102 and 4122	2888 2888 to 2482 2482 and 2450 2437 and 2426
3	Spectrum continuous to ..... <b>Absorption band</b> ..... Weak spectrum from..... Complete absorption beyond.	3474 3474 to 3994 3994 to 4172	2878 2878 to 2503 2503 to 2396
2	Spectrum continuous to ..... <b>Absorption band</b> ..... Faint spectrum from ..... Complete absorption beyond.	3488 3488 to 3994 3994 to 4172	2871 2871 to 2508 2503 to 2396
1	Spectrum continuous to ..... <b>Absorption band</b> ..... Strong line transmitted at ..... Continuous spectrum from ..... Complete absorption beyond.	3503 3503 to 3877 3911 3997 to 4172	2854 2854 to 2579 2556 2501 to 2396

0.135 gram (1 milligram-mol.) in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to ..... <b>Absorption band</b> ..... Strong line transmitted at ..... Continuous spectrum from..... Complete absorption beyond.	3512 3512 to 3812 3812 3877 to 4215	2847 2847 to 2628 2628 2579 to 2372
3	Spectrum continuous to ..... <b>Absorption band</b> ..... Continuous spectrum from ..... Spectrum continuous to .....	3524 3524 to 3812 3812 to 4240 3559	2837 2837 to 2628 2628 to 2358 2809
2	<b>Absorption band</b> ..... Strong lines feebly transmitted at ..... Continuous spectrum from .....	3559 3559 to 3780 3829 and 3885 3780 to 4240	2809 to 2645 2755 and 2718 2809 to 2358
1	Spectrum continuous to ..... <b>Absorption band</b> ..... Strong line feebly transmitted at ..... Continuous spectrum from..... Lines partially transmitted at.....	3629 3629 to 3780 3685 3780 to 4320 4355 and 4414 4540 and 4555	2755 2755 to 2645 2718 2755 to 2314 2296 and 2265 2202 and 2195

*o*-Oxycarbanil Ethyl Ether. Ketonic form; *m. p.* 29°.



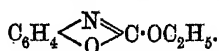
0.163 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to .....	3386	2953
	Complete absorption beyond.		
20	Spectrum continuous to .....	3390	2949
	Complete absorption beyond.		
15	Spectrum continuous to .....	3400	2941
	Complete absorption beyond.		
10	Spectrum continuous to .....	3414	2929
	Complete absorption beyond.		
5	Spectrum continuous to .....	3430	2915
	Absorption band.....	3430 to 4115	2915 to 2430
	Complete absorption beyond.		
4	Spectrum continuous to .....	3450	2898
	Absorption band.....	3450 to 4033	2898 to 2479
	Rays very feebly transmitted from .....	4033 to 4125	2479 to 2424
	Complete absorption beyond.		
3	Spectrum continuous to .....	3450	2898
	Absorption band.....	3450 to 4002	2898 to 2498
	Rays feebly transmitted from.....	4002 to 4125	2498 to 2424
	Complete absorption beyond.		
2	Spectrum continuous to .....	3478	2875
	Absorption band.....	3478 to 4002	2875 to 2498
	Very feeble line at .....	3886	2573
	Rays transmitted from.....	4002 to 4125	2498 to 2424
1	Spectrum continuous to .....	3478	2875
	Absorption band.....	3478 to 3886	2875 to 2573
	Rays transmitted from.....	3886 to 4125	2573 to 2424

0.163 gram (1 milligram-mol.) in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to .....	3434	2870
	Absorption band.....	3434 to 3820	2870 to 2617
	Spectrum feebly transmitted from.....	3820 to 4125	2617 to 2424
3	Spectrum continuous to .....	3512	2847
	Absorption band.....	3512 to 3820	2847 to 2617
	Spectrum transmitted from.....	3820 to 4122	2617 to 2426
2	Spectrum continuous to .....	3524	2837
	Absorption band.....	3524 to 3816	2837 to 2620
	Lines transmitted feebly at .....	3623 and 3748	2756 and 2668
	Spectrum transmitted from.....	3816 to 4122	2620 to 2426
1	Spectrum continuous to .....	3563	2806
	Absorption band.....	3563 to 3748	2806 to 2668
	Lines transmitted at .....	3632 and 3688	2753 and 2711
	Spectrum continuous from.....	3748 to 4176	2668 to 2394
	Spectrum transmitted continuously after further dilution.		

*o*-Oxycarbanil Ethyl Ether. Enolic form; b. p. 225—230°.



0.163 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to ..... Complete absorption beyond.	3474	2878
20	Spectrum continuous to ..... Complete absorption beyond.	3486	2868
15	Spectrum continuous to ..... Complete absorption beyond.	3524	2837
10	Spectrum continuous to ..... Complete absorption beyond.	3528	2834
5	Spectrum continuous to ..... Complete absorption beyond.	3539	2825
4	The same as 5.		
3	Spectrum continuous to ..... Complete absorption beyond.	3568	2802
2	The same as 3, but stronger.		
1	Spectrum continuous to ..... <b>Absorption band</b> ..... Spectrum faintly transmitted from.....	3568 3568 to 3885 3885 to 4033	2802 2802 to 2574 2574 to 2479

0.163 gram (1 milligram-mol.) in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to ..... <b>Absorption band</b> ..... Spectrum faintly transmitted from.....	3568 3568 to 3820 3820 to 4109	2802 2802 to 2617 2617 to 2438
3	Spectrum continuous to ..... <b>Absorption band</b> ..... Rays transmitted from.....	3632 3632 to 3820 3820 to 4125	2753 2753 to 2617 2617 to 2424
2	Spectrum continuous to ..... but feebly transmitted in the region of the absorption band.	4125	2424
1	The same spectrum, but somewhat stronger.		

LXXVIII.—*Ultra-violet Absorption Spectra of Some Closed Chain Carbon Compounds. Part II. Dimethylpyrazine, Hexamethylene, and Tetrahydrobenzene.*

By WALTER NOEL HARTLEY, F.R.S., and JAMES J. DOBBIE, D.Sc., M.A.

IN a former paper (Trans., 1898, 73, 598), we gave the results of the examination of the absorption spectra of thiophen, pyrrole, furfuran, and some of the more important furfuran derivatives. Each of these compounds contains two pairs of carbon atoms doubly linked, the chain being closed by a polyvalent element other than carbon. No trace of selective absorption, such as is shown by benzene, pyridine, and many of their derivatives, could be detected in the spectra of any of these substances.

We have now extended our investigation to 2:5-dimethylpyrazine,



a substance in which not merely one carbon is replaced by nitrogen in the benzene ring, as in pyridine, but two. It thus belongs to a group not previously examined.

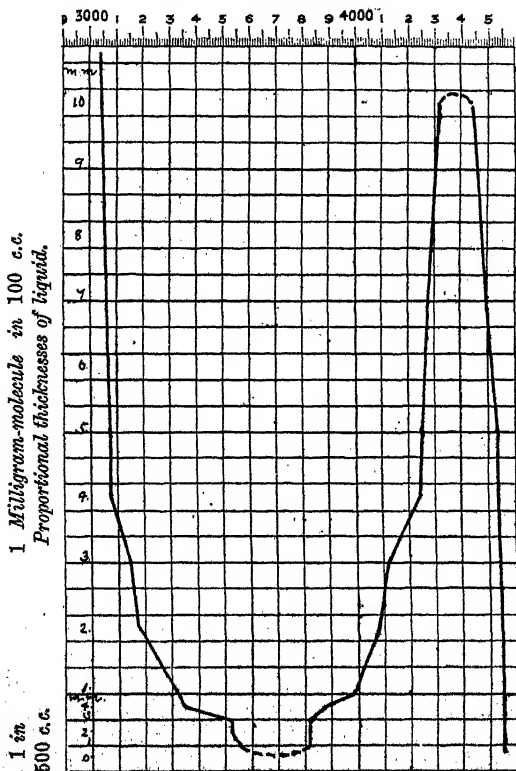
From the analogy between the constitution of this substance and that of pyridine, it was anticipated that it would show a marked selective absorption, and this anticipation proved to be correct. One of the principal reasons for examining a substance of this constitution lay in the fact that whilst pyridine contains the group  $\cdot\text{C}:\text{N}$  once in the benzene structure, dimethylpyrazine contains it twice, and the original formula proposed for cyanuric acid (Trans., 1882, 41, 84) contains it three times; accordingly, if this formula were correct for cyanuric acid and its esters, we should expect that they would exhibit a powerful absorption band, more intense than that of pyrazine, just as that of pyrazine is more intense than that of pyridine. But it has been concluded, from a widely extended experience of the behaviour of such substances under the ultra-violet rays, and particularly from the results of a recent examination of the absorption spectra of its derivatives (Hartley, *Proc.*, 1899, 15, 46), that cyanuric acid does not possess this structure, but one in which

the acid is represented by a ring composed of three  $\begin{array}{c} \cdot\text{N} \cdot \text{C} : \text{O} \\ | \\ \text{H} \end{array}$  groups, made of single linking resembling that of a hydropyridine or of a heterocyclic aromatic group with one carbon replaced by nitrogen (*Phil.*

*Trans.*, Part II, 1885, 519); it should not therefore exhibit selective absorption.

The specimen of dimethylpyrazine used in the experiments was prepared by the reduction of isonitrosoacetone in accordance with the directions given by Gabriel and Pinkus (*Ber.*, 1893, 26, 2206). It boiled constantly at 154–155° (corr.) under atmospheric pressure.

*Scale of oscillation frequencies.*



*2:5-Dimethylpyrazine.  
Curves of Molecular Vibrations.*

A layer, 25 mm. thick, of a solution of dimethylpyrazine containing 1 mill.-mol. in 100 c.c. of absolute alcohol cuts off all rays beyond  $1/\lambda$  2994. On reducing the thickness of the layer to 10 mm., an absorption band makes its appearance, reaching from  $1/\lambda$  3064 to  $1/\lambda$  4321. This band is very persistent, and is still traceable in a layer 1 mm. thick of a solution containing 1 mill.-mol. of the

substance dissolved in 500 c.c. alcohol. The band of dimethylpyrazine is thus both wider and also more persistent than that of pyridine. These results are shown in the curve on page 847.

In the paper already referred to, an account was also given of the absorption spectra of diketohexamethylene. Previous investigations had shown that piperidine (Hartley, Trans., 1885, 47, 691) and hexachlorobenzene (Hartley, Trans., 1881, 39, 153) exhibit continuous absorption, but show no absorption band, and, as was to be expected, diketohexamethylene, in which the six carbon atoms are united with each other by a single bond, as in hexachlorobenzene and piperidine, likewise showed no bands in the spectrum.

Through the kindness of Prof. Sydney Young and Miss Fortey, we have recently been enabled to examine a specimen of pure hexamethylene prepared from Galician petroleum. This substance, in comparison with benzene and pyridine, is highly diactinic. A layer, 60 mm. thick, of a solution containing 1 mill.-mol. dissolved in 20 c.c. of alcohol, transmits all rays up to  $1/\lambda$  3920, whilst a layer of the same solution, 10 mm. thick, transmits practically the whole spectrum. In none of the photographs of the spectra of this substance could any trace of a banded structure be detected.

Professor Young and Miss Fortey were also good enough to place a specimen of pure tetrahydrobenzene in our hands for examination. This substance exhibits somewhat greater general absorption than hexamethylene, a layer, 60 mm. thick, of a solution containing 1 mill.-mol. in 20 c.c. alcohol absorbing all rays beyond  $1/\lambda$  3694, while absorption is still traceable in a layer of the same solution 1 mm. thick. Like hexamethylene, tetrahydrobenzene shows no selective absorption. The examination of these two substances thus confirms the conclusion previously reached, that the banded spectrum is shown only by substances which possess the true benzenoid structure (Hartley, Trans., 1881, 39, 153).

*Dimethylpyrazine, C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>.*

0.108 gram (1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
25	Spectrum continuous to ..... Complete absorption beyond.	2994	3340
20	Spectrum continuous to ..... Complete absorption beyond.	2994	3340
15	The same.		

0.108 gram (1 milligram-mol.) in 100 c.c alcohol (*continued*).

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
10	Spectrum continuous to .....	3064	3263
	<b>Absorption band</b> .....	<b>3064 to 4321</b>	<b>3263 to 2314</b>
	Strong rays transmitted from 4321 to .....	4443	2314 to 2250
5	Spectrum continuous to .....	3076	3250
	<b>Absorption band</b> .....	<b>3076 to 4242</b>	<b>3250 to 2357</b>
	Strong rays transmitted partially from 4242 to.....	4539	2357 to 2203
	Complete absorption beyond.		
4	Spectrum continuous to .....	3076	3250
	The same as 5, excepting a faint transmission of rays at .....	4112 and 4128	2431 and 2422
3	Spectrum continuous to .....	3148	3176
	<b>Absorption band</b> .....	<b>3148 to 4112</b>	<b>3176 to 2431</b>
	Spectrum transmitted from 4112 to ...	4555	2431 to 2195
	Complete absorption beyond.		
2	Spectrum continuous to .....	3188	3186
	<b>Absorption band</b> .....	<b>3188 to 4089</b>	<b>3186 to 2445</b>
	Spectrum continuous, but weak from 4089 to.....	4555	2445 to 2195
	Complete absorption beyond.		
1	Spectrum continuous to .....	3319	3012
	<b>Absorption band</b> .....	<b>3319 to 3999</b>	<b>3012 to 2500</b>
	Weak spectrum from 3999 to .....	4555	2500 to 2195
	Complete absorption beyond.		

*Dimethylpyrazine (continued).*

0.108 gram (1 milligram-mol.) in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
4	Spectrum continuous to ... ..	3349	2985
	<b>Absorption band</b> .....	<b>3349 to 3877</b>	<b>2985 to 2579</b>
	Rays faintly visible between .....	3382 and 3438	2956 and 2871
	Spectrum ends at .....	3999	4555
3	Spectrum continuous to .....	3520	2840
	<b>Absorption band</b> .....	<b>3520 to 3818</b>	<b>2840 to 2619</b>
	Faint transmission of a strong line at .....	3818	2619
	Continuous spectrum from 3877 to.....	4555	2579 to 2195
2	Spectrum continuous to .....	3520	2840
	<b>Absorption band</b> .....	<b>3520 to 3816</b>	<b>2840 to 2620</b>
	Continuous spectrum 3816 to .....	4555	2620 to 2195
1	Spectrum continuous to .....	3563	2806
	Strong lines feebly transmitted to .....	3748	2668
	<b>Absorption band</b> .....	<b>3563 to 3816</b>	<b>2806 to 2620</b>
	Continuous spectrum 3816 to .....	4555	2620 to 2195
	Transmission of a continuous spectrum on further dilution of solution.		

*Hexamethylene, C<sub>6</sub>H<sub>6</sub>·H<sub>6</sub>.*

0.084 gram (1 milligram-mol.) in 20 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
60	Spectrum continuous to.....	3920	2551
	Complete absorption beyond, except for the feeble transmission of strong lines at.....	4112	2431
	and	4125	2424
45	Spectrum continuous to.....	4125	2424
	Faint prolongation to.....	4413	2266
30	The same as 45.		
25	The same as 30, but stronger; lines transmitted faintly at .....	4540	2202
	and	4555	2195
20	Spectrum continuous to.....	4555	2195
	But faint beyond.....	4413	2266
15	The same as 20.		
10	Spectrum continuous to .....	4555	2195
	A strong line feebly transmitted at .....	4656	2147
5	The same as 10.		
4	Spectrum continuous.		

*Tetrahydrobenzene, C<sub>6</sub>H<sub>6</sub>·H<sub>4</sub>.*

0.082 gram (1 milligram-mol.) in 20 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$ .	$\lambda$ .
60	Spectrum continuous to.....	3694	2707
45	Same as 60.		
30	Spectrum continuous to.....	3886	2573
25	" " .....	3892	2569
20	" " .....	3921	2550
15	" " .....	4029	2482
10	" " .....	4125	2424
5	Same as 10; very feeble prolongation to.....	4321	2314
4	Same as 5; " " .....	4413	2266
3	Same as 4, but somewhat stronger.		
2	Spectrum continuous to.....	4413	2266
	Strong lines transmitted at .....	4586	2205
	and	4555	2195
1	The same, but somewhat stronger.		

We have to express our indebtedness to Lieut. Horatio Nelson, R.A., of the University College of North Wales, Bangor, for his assistance in the work of this research.



LXXIX.—*The Constitution of Pilocarpine. Part I.*

By HOOPER ALBERT DICKINSON JOWETT, D.Sc.

IN a previous communication (this vol., 494), it was shown that the constitutional formula previously proposed for pilocarpine by Hardy and Calmels must be abandoned, and an account was given of certain preliminary experiments on the constitution of isopilocarpine. Since then, Pinner and Kohlhammer (*Ber.*, 1900, 33, 1424) have confirmed these conclusions, and have described several compounds of pilocarpine with bromine, as well as a new crystalline product, bromocarpinic acid,  $C_{10}H_{15}O_4N_2Br$ . The present paper contains a full account of the isolation and identification of the products formed by the oxidation of isopilocarpine with permanganate, and of the reactions of the base with soda lime, fused caustic potash, and methyl iodide.

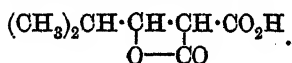
In attacking the problem of the constitution of pilocarpine, two difficulties are encountered, first, the remarkable stability of isopilocarpine towards many reagents, for example, caustic potash or nitric acid, and secondly, the high price of the alkaloid, which renders it necessary to work with small quantities of material. Although it is not yet possible to propose a formula for the alkaloid, yet, from the results recorded in this paper, the existence of certain groups in the molecule can be shown to be highly probable.

From the fact that isopilocarpine only with difficulty forms salts with metallic hydroxides, such as sodium, barium, and copper hydroxides, as well as from its behaviour towards hot alkali, it is legitimate to conclude that it contains a lactone group. In many reactions, the nitrogen is eliminated as ammonia and methylamine, and when isopilocarpine methiodide is treated with caustic potash, methylamine alone is formed. Di-alkyl derivatives of isopilocarpine could not be prepared, thus confirming Chastaing's observation (*Compt. rend.*, 1885, 101, 507), and since methyl iodide may be supposed to act as an acid towards a base, it must be assumed that of the two nitrogen atoms, the one which confers the basic character on isopilocarpine is evolved as ammonia, whilst the other is split off as methylamine, and does not act as basic nitrogen. Herzig and Meyer (*Monats.*, 1898, 19, 56) have stated that one methyl group is attached to a nitrogen atom, and since methylisopilocarpine cannot be further methylated, it must be inferred that the nitrogen atoms occur as  $:NH$  and  $:N \cdot CH_3$ , the former being that to which the basic character of isopilocarpine is due.

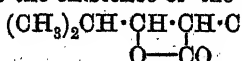
Further, the facts, that isopilocarpine is stable towards acids or alkalis and at high temperatures, and that when methylisopilocarpine

methiodide is decomposed by potash, methylamine and not dimethylamine is formed, show that these groups are attached to the rest of the molecule by a much stronger affinity than is the case in tropine, in which, by similar reactions, the nitrogen atom is eliminated, after successive methylations, as trimethylamine by simple heating with water. By distillation of isopilocarpine with soda-lime, a picoline, probably 3-methylpyridine, is formed in addition to ammonia and methylamine, but only in very small quantity. As the preparation of a sufficient quantity of the methylpyridine for its complete identification would have necessitated the use of large quantities of valuable material, and as its production in such small quantity, by so drastic a reaction, would not afford much clue to the constitution of the alkaloid, the investigation of this reaction was not further pursued.

By oxidation with permanganate, in addition to acetic acid, an acid,  $C_7H_{10}O_4$ , has been isolated, which proved on titration to be lactonic. It was not identical with any acid of this formula previously described, but, from the fact that the corresponding unsaturated dibasic acid yielded isobutyric acid on ultimate oxidation, the most probable formula would appear to be



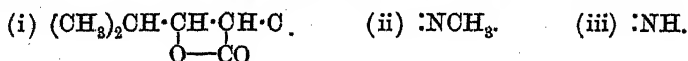
This would necessitate the existence of the complex



in isopilocarpine.

The formation of isobutyric acid by fusion of isopilocarpine with caustic potash, which is proved in this paper, and the lactonic nature of the alkaloid would thus be explained.

The results of the present investigation therefore indicate the existence of the following groups in pilocarpine and isopilocarpine:



#### EXPERIMENTAL.

##### *Distillation of Isopilocarpine with Soda Lime.*

Four grams of isopilocarpine nitrate were treated with 50 grams of soda-lime as previously described (*loc. cit.*, 494), and the ammonium salt separated from the hydrochlorides soluble in absolute alcohol. The latter were dissolved in water, excess of auric chloride added, and the crystalline precipitate recrystallised from hot dilute hydrochloric acid. The filtrate from the precipitated aurichloride contained methylamine, which was isolated as the platinichloride and analysed.

0.0358 fused on heating and gave 0.0148 Pt. Pt = 41.34.

$(\text{CH}_3 \cdot \text{NH}_2)_2 \cdot \text{H}_2\text{PtCl}_6$  requires Pt = 41.3 per cent.

The aurichloride, amounting to less than 0.2 gram, melted at  $185-187^\circ$  (corr.), contained Au = 45.71 per cent. (methylpyridine aurichloride requires Au = 45.64 per cent.), and yielded a crystalline picrate which melted at about  $130^\circ$ , and a crystalline platinichloride melting indistinctly at  $200^\circ$ . When oxidised with permanganate, an acid was formed which gave a precipitate with copper acetate, but no coloration with ferrous sulphate; the quantity obtained was too small to admit of identification. These properties agree best with those of 3-methylpyridine.

The bases formed by distillation with soda-lime, therefore, are ammonia and small amounts of methylamine and (probably 3-) methylpyridine.

#### *Interaction of Isopilocarpine with Methyl Iodide.*

As isopilocarpine under certain conditions loses ammonia, and as it forms a methiodide, experiments were undertaken similar to those carried out on tropine (Merling, *Ber.*, 1891, 24, 3108) to see whether, by successive methylation, the hydrogen atoms attached to the nitrogen could be replaced by methyl, and possibly some of the bonds broken. Pure isopilocarpine methiodide was treated with the theoretical amount of moist silver oxide and filtered, a solution of isopilocarpine methyl-hydroxide being obtained, which gave no precipitate on the addition of picric acid or platinic chloride. After boiling with these reagents and cooling, crystalline salts separated, however, and the same result was obtained if the solution of the methyl hydroxide was previously boiled with dilute hydrochloric acid. On boiling, therefore, isopilocarpine methyl-hydroxide loses water, becoming converted into methyl-isopilocarpine, which is capable of forming salts.

*Methylisopilocarpine Picrate* crystallises in beautiful, orange needles from hot water or alcohol, being sparingly soluble in these solvents at the ordinary temperature. The crystals melt sharply at  $136^\circ$  (corr.) to a clear liquid, and the melting point is not altered by further recrystallisation.

*Methylisopilocarpine Platinichloride* is obtained in well shaped, orange cubes which melt sharply at  $218^\circ$  (corr.) to a clear liquid without decomposition. It can be recrystallised from hot acidified water. On analysis:

0.1846 gave 0.0422 Pt. Pt. = 22.87.

0.2494 „ 0.0572 Pt. Pt. = 22.93.

$[\text{C}_{11}\text{H}_{15}(\text{CH}_3)_2\text{O}_2\text{N}_2]_2 \cdot \text{H}_2\text{PtCl}_6$  requires Pt = 22.87 per cent.

The hydrochloride was obtained by boiling the methyl-hydroxide with dilute hydrochloric acid, but neither this salt nor the nitrate has yet been crystallised. The base is soluble in water but insoluble in chloroform, thus differing from isopilocarpine, which is miscible with this solvent.

Methylisopilocarpine was heated with excess of methyl iodide, and the latter removed by distillation; the syrupy residue was then treated with moist silver oxide and filtered. After boiling with dilute hydrochloric acid, it yielded a crystalline picrate and platinichloride melting at  $129^{\circ}$  and  $213^{\circ}$  respectively, or a few degrees lower in each case than the corresponding salts of methylisopilocarpine. On analysis, it was found that further methylation had not taken place and that the base was unaltered methylisopilocarpine.

0.225 platinichloride gave 0.0514 Pt. Pt = 22.84.

$[C_{11}H_{15}(CH_3)O_2N_2]_2 \cdot H_2PtCl_6$  requires Pt = 22.87 per cent.

Further heating with methyl iodide and subsequent decomposition produced a similar result, the platinichloride melting at  $212^{\circ}$  and containing Pt = 22.54 per cent. It follows therefore that by the action of methyl iodide only monomethylisopilocarpine can be produced.

The methiodide prepared as above, was treated with 20 per cent. caustic potash solution in a sealed tube for 4 hours at  $150^{\circ}$ , and the volatile bases collected and converted into the hydrochloride. The salt was entirely soluble in absolute alcohol and was precipitated in four fractions with platinic chloride. These platinichlorides were analysed with the following results:

Fraction 1. 0.2226 gave 0.0916 Pt. Pt = 41.15.

" 2. 0.3258 " 0.134 Pt. Pt = 41.13.

" 3. 0.1788 " 0.074 Pt. Pt = 41.38.

" 4. 0.1654 " 0.0688 Pt. Pt = 41.59.

$(CH_3-NH_2)_2 \cdot H_2PtCl_6$  requires Pt = 41.3 per cent.

The base was therefore homogeneous and was methylamine.

The explanation of these results would seem to be that there exists in isopilocarpine the group  $\cdot NH$ , which reacts with methyl iodide, forming  $R \cdot NH \cdot CH_3I$ ; this with moist silver oxide yields  $R \cdot NH \cdot CH_3 \cdot OH$ , which on boiling with dilute acids loses water and forms  $R \cdot N \cdot CH_3$ .

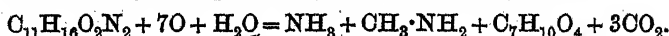
The methylated base can react with methyl iodide, forming  $R \cdot NCH_3 \cdot CH_3I$ , but on further treatment, the methyl iodide is eliminated, leaving the original base  $R \cdot NCH_3$ . With caustic potash, the nitrogen of this complex is eliminated as methylamine, together with the same base formed from the other nitrogen group.

The non-basic product of the action of potash on methylisopilocarpine is under investigation.

Nitrous acid appears to have no action on isopilocarpine.

*Oxidation of Isopilocarpine with Permanganate.*

In the preliminary account of this reaction (*loc. cit.*), it was shown that the bases formed were ammonia and methylamine, and that two oils had been isolated, one having the properties of a lactone. Further investigation has shown that, in addition to a small quantity of acetic acid, an almost theoretical yield of a new acid,  $C_7H_{10}O_4$ , is obtained. Experiments were made with varying amounts of permanganate, but the best results were obtained when 6 molecular proportions were used, the yield then amounting to 70 per cent. of the theoretical. The reaction may be expressed by the following equation:



The details of one experiment may be given. Fifty-four grams of pure isopilocarpine nitrate, dissolved in a litre of water, were oxidised at  $80^\circ$  by the gradual addition of 188 grams of permanganate dissolved in 5 litres of water, the whole being kept thoroughly stirred by a turbine. The manganese dioxide was removed by filtration and thoroughly washed with hot water, the colourless filtrate and washings evaporated to a low bulk, made alkaline with caustic soda, and then distilled until the distillate was no longer alkaline. The residue was neutralised with hydrochloric acid, evaporated to dryness, mixed with sand, thoroughly dried, and then extracted with hot absolute alcohol in a Soxhlet apparatus. The alcoholic liquid, after saturation with hydrogen chloride, was allowed to stand, then boiled in a reflux apparatus for 2 hours, and distilled on the water-bath.

The distillate had the distinct odour of ethyl acetate, so the first fractions were collected separately. The residue, after removal of the alcohol by distillation, was thrown into water, the acid liquid extracted several times with ether, the ethereal liquid washed with water until free from acid, dried over calcium chloride, and distilled to remove the ether.

The first fraction distilled from the alcoholic solution was hydrolysed with caustic potash, and the alcohol removed by evaporation; the residue was then dissolved in water, acidified with dilute sulphuric acid, and distilled. The crystalline barium salt obtained from the acid distillate was converted into the crystalline silver salt by treatment with silver nitrate solution, and on analysis the following result was obtained:

0.0584 gave 0.0376 Ag.  $Ag = 64.4$ .

$C_7H_5O_2Ag$  requires  $Ag = 64.67$  per cent.

The acid was therefore *acetic acid*, and examination of the other portions of the alcoholic distillate failed to reveal the presence of any other acid.

The ethereal residue was fractionated first in a vacuum and finally under atmospheric pressure, the following fractions being obtained :

1. Boiling at 280—299°. Yield = 5 per cent.
2. " " 299° " = 90 "
3. " " 200—210° under 10 mm. pressure. Yield = 5 per cent.

The liquid boiling at 299° was therefore pure, and on further fractionation was found to distil almost completely at this temperature. It was quite free from nitrogen. Analyses were made of a number of specimens, with the following results :

1. 0.1608 gave 0.34 CO<sub>2</sub> and 0.1106 H<sub>2</sub>O. C = 57.83; H = 7.65.
  2. 0.1822 " 0.393 CO<sub>2</sub> " 0.1266 H<sub>2</sub>O. C = 58.83; H = 7.72.
  3. 0.22 " 0.4712 CO<sub>2</sub> " 0.153 H<sub>2</sub>O. C = 58.41; H = 7.73.
  4. 0.239 " 0.511 CO<sub>2</sub> " 0.164 H<sub>2</sub>O. C = 58.32; H = 7.62.
- C<sub>9</sub>H<sub>14</sub>O<sub>4</sub> requires C = 58.07; H = 7.53 per cent.

The specific rotation of the pure liquid was determined with the following result :

$$\alpha_{15} = +22^\circ; l = 50 \text{ mm.}; d_{15}^{15} = 1.1053; [\alpha]_D^{15} = +39.8^\circ.$$

The liquid was insoluble in water, but soluble in ether or alcohol, and had a peculiar, but not unpleasant, smell. On hydrolysis, it was found to be the ethyl ester of a dibasic or lactonic acid, as with phenolphthalein as indicator it required 2 molecular proportions of alkali to effect neutralisation.

*Acid C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>, formed by Oxidation.*

The acid was formed from the ester by hydrolysing either with caustic potash or aqueous hydrochloric acid. It is a thick, slightly yellow oil which does not solidify at -21°, boils at 210—220° under 10 mm. pressure, and is freely soluble in water, ethyl alcohol, or benzene. All attempts to crystallise it failed. On analysis :

- 0.1826 gave 0.3514 CO<sub>2</sub> and 0.1094 H<sub>2</sub>O. C = 52.48; H = 6.65.  
C<sub>7</sub>H<sub>10</sub>O<sub>4</sub> requires C = 53.16; H = 6.33 per cent.

When titrated in the cold with *N*/10 alkali, using phenolphthalein as indicator, 0.1678 required 10.7 c.c. *N*/10 alkali. Calculated 10.6 c.c. When titrated by boiling, first with excess of alkali, and then titrating back with acid, while still hot, 0.2234 required 26.00 c.c. *N*/10 alkali. Calculated 28.2 c.c.

The acid is therefore lactonic, and the formula may be written



A neutral solution of the potassium salt gave white, gelatinous precipitates with lead acetate and silver nitrate, the precipitate with the latter undergoing slow reduction. It gave no reaction with barium or calcium chloride, or copper acetate.

*Formation of the Unsaturated Diethyl Ester.*

A preliminary experiment having shown that phosphorus pentabromide reacted with the ethyl ester, the whole of the ester at disposal was treated in this way. Twelve grams of the ester and 60 grams of phosphorus pentabromide were placed in a reflux apparatus, and, after the pasty mass had gradually liquefied, the whole was gently heated. Ethyl bromide was first given off, and then hydrogen bromide. As the object of the reaction was to obtain, not the bromo-derivative, but the unsaturated ester, the heating was continued until no more hydrogen bromide was evolved. The product was then gradually added to an excess of absolute alcohol, warmed to remove ethyl bromide, poured into ice-cold water, and the aqueous liquid extracted several times with ether. The ethereal solution, after washing with water, was dried over calcium chloride and distilled. In this way, 16.6 grams of crude product was obtained, which was fractionated in a vacuum. Considerable difficulty was experienced during distillation owing to frothing of the liquid, but ultimately three fractions were obtained, boiling respectively at 165—170°, 170—195°, and 195—200° under 20 mm. pressure. There were thus at least two substances present, so the first and third fractions were examined.

The *first fraction* (b. p. 165—170°) contained a large amount of bromine, but also instantly decolorised cold alkaline permanganate solution. It consisted chiefly of the bromoethyl ester, with a small quantity of the unsaturated compound. On analysis, the following results were obtained:

0.1702 gave 0.293 CO<sub>2</sub> and 0.097 H<sub>2</sub>O. C = 46.94; H = 6.34.

C<sub>5</sub>H<sub>9</sub>Br(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> requires C = 44.74; H = 6.44 per cent.

The *third fraction* (b. p. 195—200°) contained bromine and readily decolorised cold alkaline permanganate. It consisted chiefly of the unsaturated ethyl ester, and on analysis gave the following result:

0.2934 gave 0.0654 AgBr. Br = 9.5.

C<sub>11</sub>H<sub>19</sub>BrO<sub>4</sub> requires Br = 27.1 per cent.

In order to complete the debromination, the whole of the liquid was heated with two molecular proportions of diethylaniline in a reflux apparatus on a sand-bath for 13 hours, when, on cooling, crystals of diethylaniline hydrobromide separated. The coloured liquid was then poured into excess of dilute hydrochloric acid and extracted with

ether. The ethereal solution was washed successively with dilute acid, dilute sodium carbonate solution, and water, dried over calcium chloride, and the ether removed by distillation. The residue was distilled in a vacuum, and on fractionation the greater part came over at  $155^{\circ}$  under 10 mm. pressure, a small quantity of a liquid of higher boiling point being apparently present.

*Hydrolysis of the Unsaturated Ester and Oxidation of the Acid.*

As the quantity of the ester was insufficient to admit of satisfactory fractionation, the unsaturated acid was isolated, purified as far as possible, and then oxidised by Crossley and Le Sueur's method (Trans., 1899, 75, 161), in the hope that identification of the products of oxidation would give a clue to the constitution of the acid.

The ester boiling at  $155^{\circ}$  under 10 mm. pressure was dissolved in methyl alcohol and treated with an equal weight of caustic potash in methyl alcoholic solution. On the addition of alkali, a red colour was produced, changing to brown. The alcoholic liquid was heated on a water-bath for  $2\frac{1}{2}$  hours in a reflux apparatus, the alcohol removed by evaporation, and the residue acidified and extracted with ether. The ethereal solution, after washing with water, was dried over calcium chloride, and allowed to evaporate spontaneously. No crystals separated, but a light coloured oil was obtained, having the odour of a fatty acid. The oil distilled between  $180^{\circ}$  and  $200^{\circ}$  under 10 mm. pressure, and dissolved in sodium carbonate solution with effervescence; this solution at once decolorised permanganate at the ordinary temperature, thus affording proof of its unsaturated character (von Baeyer, *Annalen*, 1888, 245, 146). On oxidation with cold permanganate, the acid required 98 c.c. *N*/10 solution (calculated 110 c.c.). After removal of the manganese dioxide, the filtrate was oxidised by chromic acid, distilled with steam and the volatile acid, which smelt strongly of a butyric acid, converted into the silver salt. On analysis, the following result was obtained:

0.126 gave 0.111  $\text{CO}_2$ ; 0.037  $\text{H}_2\text{O}$ ; and 0.069 Ag.  $\text{C} = 24.05$ ;  
 $\text{H} = 3.26$ ;  $\text{Ag} = 54.76$ .

$\text{C}_4\text{H}_7\text{O}_2\text{Ag}$  requires  $\text{C} = 24.61$ ;  $\text{H} = 3.59$ ;  $\text{Ag} = 55.38$  per cent.

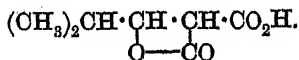
The neutral solution gave a precipitate with calcium chloride which dissolved on warming, and separated on cooling.

The acid, therefore, is isobutyric acid; the amount is small, but additional indirect proof of its identity is furnished by the fact that isobutyric acid is formed by fusion of pilocarpine with potash.

The reactions with phosphorus pentabromide and diethylaniline seem to prove conclusively the lactonic nature of the acid  $\text{C}_7\text{H}_{10}\text{O}_4$ , and since it does not agree with any of the known lactonic acids of

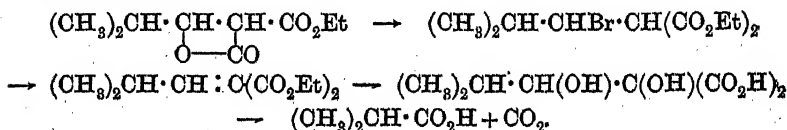


this composition, the formation of isobutyric acid would leave only one formula possible, namely,



The stability of the compound is remarkable, if it is the lactone of a  $\beta$ -hydroxymalonic acid; the formation of isobutyric acid, however, does not admit of the possibility of its being a  $\gamma$ -lactone, for if that were the case, acetone should be formed on oxidation, whereas careful search failed to detect it.

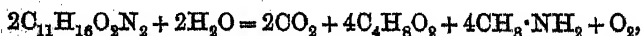
The reactions described in the preceding paragraphs may be represented as follows:



Experiments were made with pilocarpine to obtain the bromoethyl ester, by treatment with phosphorus pentabromide, but the basic character of pilocarpine interfered with the reaction, and a negative result was obtained.

#### *Fusion of Isopilocarpine with Caustic Potash.*

Chastaing (*Compt. rend.*, 1882, 94, 223) has described the fusion of pilocarpine with caustic potash, and stated that the products of the reaction were methylamine, carbon dioxide, butyric acid, and traces of acetic acid, and that the reaction may be represented by the equation



The analytical numbers quoted for the platinichloride\* prove, however, that he was working with a mixture of ammonia and methylamine, and no details are given of the identification of butyric or acetic acids.

In the preliminary account of this reaction (*loc. cit.*, 496), the bases formed were proved to be ammonia and methylamine, and the acids yielded a silver salt, which contained a higher percentage of silver than required for silver butyrate. The reaction has been further investigated. Five grams of pure isopilocarpine were fused with 50 grams of caustic potash, and the fused mass, after cooling, dissolved in water acidified with sulphuric acid, and distilled with

\* Found Pt = 42.5 per cent.

$(\text{NH}_3)_2, \text{H}_2\text{PtCl}_6$  requires Pt = 43.9 and  $(\text{CH}_3 \cdot \text{NH}_2)_2, \text{H}_2\text{PtCl}_6$  requires Pt = 41.3 per cent.

steam. The acid liquid was extracted with ether, the ethereal solution dried over calcium chloride, and distilled.

The residual liquid, which had a strong, rancid smell, was distilled at atmospheric pressure, when a small fraction was collected below  $120^{\circ}$ , but the greater portion came over between  $120^{\circ}$  and  $155^{\circ}$ , leaving no residue. On adding a little water to the higher fraction, oily drops separated, which dissolved on the addition of more water. From the aqueous liquid, a crystalline barium salt was prepared; this was extracted with boiling alcohol, in which it was very slightly soluble.

(i) The portion dissolved by alcohol gave a white, silver salt, which was not reduced on standing. On analysis the following result was obtained:

0.0388 gave 0.0214 Ag.  $\text{Ag} = 55.2$ .

(ii) The residue after extraction with alcohol gave a crystalline silver salt, which was recrystallised from hot water. On analysis, the following result was obtained:

0.0592 gave 0.0328 Ag.  $\text{Ag} = 55.4$ .

$\text{C}_4\text{H}_7\text{O}_2\text{Ag}$  requires  $\text{Ag} = 55.38$  per cent.

The calcium salt was soluble in warm water, but separated again on cooling. The analytical numbers, boiling point, immiscibility with water, and solubility of the calcium salt, prove conclusively that the acid formed is isobutyric acid.

The portion boiling below  $120^{\circ}$  gave a small amount of an amorphous barium salt, insoluble in alcohol, and an amorphous silver salt ( $\text{Ag} = 57.4$  per cent.), which underwent reduction on standing. No trace of acetic acid could be found.

Further investigation of the subject is proceeding on different lines, and it is hoped, either by the use of larger quantities of material, or by synthetical methods, to bring forward further proof of the correctness, or otherwise, of the formula now proposed for the acid  $\text{C}_7\text{H}_{10}\text{O}_4$ .

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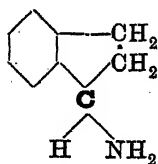
LXXX.—*Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen. Parts I—VI. Hydrindamine Bromocamphorsulphonates, Chlorocamphorsulphonates, and cis- $\pi$ -Camphanates.*

By FREDERIC STANLEY KIPPING, Ph.D., D.Sc., F.R.S.

THIS paper contains an account of the preparation and investigation of three pairs of isomeric partially racemic salts, the isomerism of which is apparently of a kind different from any yet recorded.

All these salts have been obtained from  $\alpha$ -hydrindamine,\* a primary base easily prepared by reducing  $\alpha$ -hydrindoxime (compare Revis and Kipping, *Trans.*, 1897, 71, 250).

Hydrindamine contains an asymmetric carbon group, as will be seen from its formula,



and the synthetical base is therefore composed of equal quantities of enantiomorphous components.

When this base is combined with various optically active acids, it shows an altogether unusual behaviour, giving in some cases what appears to be a homogeneous partially racemic salt, in others a mixture of unequal quantities of two isomeric salts; the latter are not the ordinary isomerides which are obtained from most externally compensated bases under such conditions, that is to say, they do not represent salts of the separate enantiomorphously related components of the base, but are both comparable to partially racemic substances.

The results of the examination of these remarkable isomerides may be briefly summarised as follows.

Hydrindamine and  $\alpha$ -bromocamphorsulphonic acid unite to form *unequal* quantities of two hydrated salts, which contain different quantities of water of crystallisation; the anhydrous salts both have the molecular formula  $C_9H_{11}N, C_{10}H_{14}BrO \cdot SO_3H$ . The more sparingly soluble " $\alpha$ -salt" separates from water in opaque, bulky masses of minute needles, whereas the more readily soluble " $\beta$ -salt" crystallises in well-defined, transparent prisms, absolutely different in appearance

\* The letter  $\alpha$ - which is used here to distinguish this base from  $\beta$ -hydrindamine is not employed again, as to do so might cause confusion with the  $\alpha$ -salts, which are described later.

from the crystals of its isomeride. The two salts have different specific rotations.

Hydrindamine and  $\alpha$ -chlorocamphorsulphonic acid unite to form unequal quantities of two isomeric salts which are respectively analogous to those of the bromo-acid; the more sparingly soluble  $\alpha$ -salt is isomeric with the corresponding bromo-salt, from which it cannot be distinguished by inspection. The  $\beta$ -chloro-salt bears a close relationship to the  $\beta$ -bromo salt, but differs from the latter in at least one important respect; when crystallised from water, it is deposited either in what may be termed the normal form of transparent, well-defined prisms, closely resembling, and doubtless isomeric with, the crystals of the  $\beta$ -bromo-salt, or it is obtained in opaque masses indistinguishable by inspection from those of the  $\alpha$ -chloro-salt; these two varieties, so different in appearance, both represent  $\beta$ -salt, and although convertible one into the other by crystallisation, undergo this change in a rather bewildering manner, and under conditions which have not yet been established. The conversion of either of these  $\alpha$ -salts (bromo- or chloro-) into the corresponding  $\beta$ -salt, or *vice versa*, by crystallisation only, has never been observed. The specific rotations of the  $\alpha$ - and  $\beta$ -chloro-salts are practically the same in dilute aqueous or alcoholic solution, but different in other solvents.

Hydrindamine and *cis*- $\pi$ -camphanic acid (Kipping, Trans., 1896, 69, 913) give apparently unequal quantities of two isomeric anhydrous salts of the composition  $C_9H_{11}N, C_{10}H_{14}O_4$ , which are indistinguishable in appearance, but differ in melting point and other properties; the more sparingly soluble  $\alpha$ -salt melts at about  $193^\circ$ , the  $\beta$ -isomeride at about  $173^\circ$ , and the two compounds seem to be partially, but slowly, converted one into the other in aqueous solution. The two isomerides have widely different specific rotations in methyl alcoholic solution, but in dilute aqueous solution they give practically the same value; the  $\alpha$ -salt shows mutarotation in a very marked manner, but apparently the  $\beta$ -salt does not.

The question now to be discussed is, how to account for the existence of these isomerides. In doing so, it will be convenient to take a particular case, such as that of the hydrindamine bromocamphorsulphonates, with which most of the experiments have been made, the behaviour of the other salts being considered only when there is some important difference to note.

The most natural conclusion, namely, that the externally compensated base is resolved into its enantiomorphous components by fractional crystallisation of its salts with these optically active acids, will first be examined, and, as evidence against this view, the fact that the isomerides are obtained in very unequal quantities may first be quoted. The base regenerated from the  $\alpha$ -salt is optically inactive, and

is identical in this, and in every respect, with the base regenerated from the  $\beta$ -salt, and also with externally compensated hydrindamine prepared directly from hydrindoxime; this is proved by the fact that the salts obtained by combining the regenerated bases with optically inactive or active substances are identical. It may therefore be concluded, provisionally, at any rate, that the externally compensated base has not been resolved into its enantiomorphous components.

Granting this to be so, the formation of the isomerides might be explained by assuming that the salts of the sulphonic acids are merely differently hydrated varieties of one substance; this is not the case, however, because these salts are not convertible one into the other by crystallisation, they have different specific rotations in aqueous solution, and the anhydrous compounds have different melting points; moreover, such an assumption would not explain the existence of the isomeric anhydrous *cis*- $\pi$ -camphanates. For similar reasons, the isomerides cannot be regarded as different crystallographic forms of one individual compound.

The view that the  $\beta$ -salts of the sulphonic acids are derived from an acid physically or chemically isomeric with the acid of the  $\alpha$ -salt might next be adopted, especially as these  $\beta$ -salts are formed in comparatively small quantities; it is shown, however, that the acid regenerated from the  $\beta$ -salt is identical with that of the  $\alpha$ -salt; also that the behaviour of the salts themselves towards ferric chloride, phenyl isocyanate, piperidine, &c., is such as to practically exclude the possibility of the existence in the  $\beta$ -salt of a tautomeric form of the acid which might change when liberated from the base: the existence of the isomeric *cis*- $\pi$ -camphanates, and many other facts, show that the isomerism is not due to the acid ion of the salts; further, the  $\beta$ -salt of any one of the acids is converted into the  $\alpha$ -salt on repeatedly evaporating it with small quantities of externally compensated hydrindamine.

As these facts seem to prove that the isomerism is due to the hydrindamine, and as the base obtained from the  $\alpha$ -salt is nevertheless identical with that regenerated from the  $\beta$ -salt, it might be assumed that the  $\alpha$ - and  $\beta$ -isomerides are actually the salts of enantiomorphously related bases, but that the latter undergo rapid racemisation at ordinary temperatures when liberated from the acid. That this explanation will not suffice is proved (a) by the fact that the salts are obtained in unequal quantities, (b) by the fact that the *cis*- $\pi$ -camphanates afford optically inactive hydrindamine hydrochloride when decomposed directly with hydrochloric acid, and (c) by the values obtained for the molecular rotations of the salts in dilute aqueous solution. These three facts may be discussed a little, as they are all of considerable importance.

With regard to (a), it is quite possible that an externally com-

pensated base might yield unequal quantities of the salts of its enantiomorphous components provided that the one salt were convertible into the other during crystallisation as in the case recently recorded by Pope and Peachey (Proc., 1900, 16, 116); but the isomeric hydrindamine bromo- and chloro-camphorsulphonates are not thus convertible one into the other; they may be repeatedly recrystallised from water or other solvents without undergoing change. In order to account for the formation of unequal quantities of the  $\alpha$ - and  $\beta$ -isomerides on the assumption that they contain enantiomorphously related basic components, it would be necessary to assume further that the one enantiomorphous base is transformed into the other in aqueous solution before it combines with the acid; manifestly, this view cannot be adopted.

The fact (b) that either of the *cis*- $\pi$ -camphanates, when directly treated with hydrochloric acid, gives an optically inactive hydrindamine hydrochloride is of importance from its bearing on this question. Admitting the ionic dissociation hypothesis, it must be concluded that the base ions of any one of the sulphonic salts, if optically active, are incapable of racemisation, as the isomerides are not mutually convertible in very dilute aqueous solution; consequently, it seems very improbable that racemisation could occur in the direct conversion of one of the *cis*- $\pi$ -camphanates into the hydrochloride, a reaction which may be regarded as a mere interchange of ions.

The fact (c) that the values of the molecular rotations of the salts exclude the assumption that the isomerides contain enantiomorphously related bases will be obvious from the following considerations.

The molecular rotation of bromocamphorsulphonic acid in aqueous solution is approximately  $[M]_D + 270$ , a value which has been established by numerous observations by Kipping and Pope (Trans., 1893, 63, 548), Walden (*Zeit. physikal. Chem.*, 1894, 15, 196), and also by some made for the purposes of this paper; this value seems to be practically independent—as it should be—of the nature of the base with which the acid may be combined, salts such as potassium, ammonium, morphine, and phenylparatolyliodonium bromocamphorsulphonates giving almost identical molecular rotations.

Now the molecular rotations of the  $\alpha$ - and  $\beta$ -bromocamphorsulphonates are  $[M]_D + 268$  and  $+ 220$  respectively, both being determined in approximately 1 per cent. aqueous solution; the former then is normal on the assumption that the base is optically inactive and that ionic dissociation is sufficiently complete to give the true value of the acid ion; the latter, however, is about 19 per cent. too low,—more than can be attributed to experimental error.

To account for this abnormal value, it might be suggested (1) that the  $\beta$ -salt contains *L*-hydrindamine, (2) that the  $\beta$ -salt contains optically

inactive base, but gives an acid ion which is not that of ordinary bromocamphorsulphonic acid, (3) that the salt is not sufficiently dissociated. The first view is untenable, because it would necessitate the further assumption that some of the *d*-hydrindamine of the externally compensated base passes into the *l*-isomeride before the base combines with the acid; also because the  $\beta$ -salt of the chloro-acid, which is doubtless very closely analogous to this  $\beta$ -bromo-salt, gives a practically normal molecular rotation—or, if not, a value which indicates the presence of a *dextrorotatory* base; also because the molecular rotations of the isomeric *cis*- $\pi$ -camphanates are both apparently normal on the assumption that they both contain optically inactive base.

The second possible explanation of the abnormal molecular rotation of the  $\beta$ -bromo-salt, namely, that this compound contains an isomeric bromocamphorsulphonic acid, has been shown to be untenable, and is further disproved by the arguments just advanced.

The third possible view is not contrary to any direct evidence, and may therefore be accepted for the present.

Reviewing the whole of the experimental evidence, it seems to be proved that the isomeric compounds in question do not represent salts of the enantiomorphously related bases, but that they all contain optically inactive, externally compensated hydrindamine.

How, then, can the existence of such isomerides be accounted for?

To assume that there are two isomeric optically inactive hydrindamines is out of the question, since the base of the  $\alpha$ -salt is identical with that of the  $\beta$ -isomeride; further, the base regenerated from the  $\alpha$ -salt gives *both* isomerides when it is again neutralised with the acid.

To assume that hydrindamine does not contain an asymmetric carbon group, and has not the constitution assigned to it, leaves the matter just where it was; moreover, the method of formation of the base, its conversion into trimethylhydrindamine iodide (Kipping and Hall, this vol., p. 467), and the decomposition of the last-named substance into indene and trimethylamine hydriodide (*loc. cit.*), are facts of such importance that there can be no hesitation in accepting the constitutional formula which has been assigned to the base above.

Since, then, it must be admitted that the isomerides are formed by the combination of one and the same externally compensated base with one and the same acid, their isomerism must be ascribed to a difference in configuration caused by the union of their identical components in different ways; further, since the isomerides are essentially different not only in the crystalline state, but also in solution, the difference in configuration must extend to their chemical molecules.

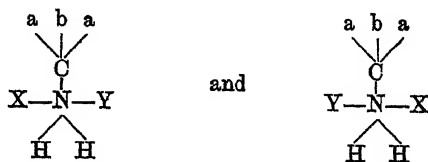
An explanation which at one time suggested itself was, that the  
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two salts were comparable to ordinary stereoisomerides. Although the nitrogen atom is only singly linked to carbon, it seemed possible that stereoisomeric forms might exist, in consequence of the great size of the acid molecule, which, by colliding with the hydrindamine ring in various directions, might limit the rotation of the nitrogen atom; since, however, the salts do not immediately change one into the other in dilute aqueous solution, when, owing to ionic dissociation, the acid ion is no longer united to the nitrogen atom, this view of their isomerism had to be abandoned.

Now, there seems to be no doubt that the isomerides are both ordinary salts, formed by the mere addition of the ions of the acid to the base; in this process, according to the usually accepted view, the two acid ions become directly united to the trivalent nitrogen atom, which then becomes quinquivalent. Two questions therefore suggest themselves in connection with this process: firstly, are the two affinities or valencies of the nitrogen atom which are concerned in such a union identically, or differently, situated with regard to the other three (which are generally regarded as arranged symmetrically in one plane)? Secondly, does the negative ion of the acid necessarily combine with or take up one particular nitrogen valency, or may it occupy either of the two which may be concerned?

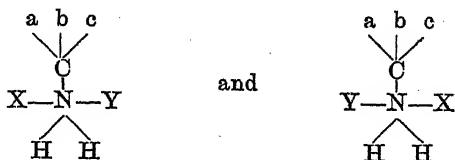
From the results of work which has been done in connection with the stereochemistry of nitrogen, definite answers to these questions cannot yet be drawn; there certainly seems to be a considerable difference of opinion in regard to the first question—which would probably determine the second,—and in any case the experimental evidence admits of no conclusive interpretation. Under these circumstances, judging by analogy with carbon—if it be permissible to do so—it seems probable that when a symmetrical primary, secondary, or tertiary base combines with an optically inactive acid or halogen alkyl compound, the ions or groups do not attach themselves to one particular nitrogen valency, but are equally distributed between two.

If this view be adopted, it will be obvious that the nitrogen atom of a base in which there is an asymmetric carbon group may show a behaviour altogether different from that of the nitrogen atom of a symmetrical compound; for, whereas in the latter case combination would naturally give rise to *equal* quantities of isomerides which may be represented by



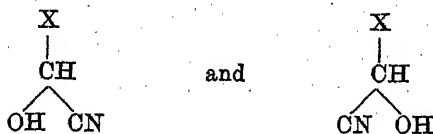


the former would probably give *unequal* quantities of the two isomerides



because of the enantiomorphous carbon group, with respect to which X and Y cannot be identically situated.

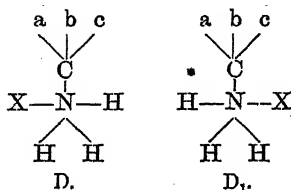
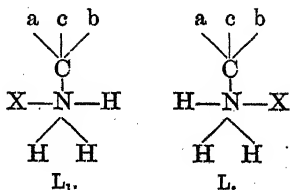
In the case of the combination of hydrogen cyanide with an aldehyde, for example, direct addition to the group  $\text{X}\cdot\text{CHO}$  takes place, and whether the forms



are produced in equal or unequal quantities depends entirely on the configuration of the part X; if this be symmetrical, equal quantities of enantiomorphously related groups are formed, but if it be asymmetrical, unequal quantities of new enantiomorphous groups are produced, and two different substances result, until possibly in extreme cases the influence of X may be sufficient to ensure the formation of only one kind of new asymmetric group.

Now, in the case of the hydroxycyanides formulated above, it is known that the two forms are enantiomorphously related so long as X is not enantiomorphous; but in the case of the supposed isomerides of the symmetrical base, it is not possible to say whether this would be so or not until it is known whether the two nitrogen valencies carrying X and Y are symmetrically situated or not with regard to the other three. When, however, an optically active base such as one of the components of externally compensated hydrindamine, combines with an optically active acid, it is obvious that the two isomerides *cannot* be enantiomorphously related, whatever the configuration of the nitrogen atom; consequently, they might be expected to differ in ordinary properties, and possibly to be separable by crystallisation.

Granting that the one component of externally compensated hydrindamine might thus give rise to two isomerides, its antipodes would naturally do so likewise, and in this way four different substances might be initially produced by the union of the base with the acid, as may be indicated by the following formulæ:

*α*-Hydrindamine.*l*-Hydrindamine.

Of these four isomerides, no two are enantiomorphously related, since the group X is common to all, and unless the directions of the three valencies of the nitrogen atom, by which it is united to carbon and to the acid ions respectively, are all situated in a plane at right angles to the plane about which the whole nitrogen group may be free to rotate, no two of these forms could become identical by such a rotation of the nitrogen atom.

These considerations lead to a possible explanation of the existence of the isomeric hydrindamine salts, which is based on two assumptions only; firstly, that the acid negative ion does not necessarily take up one particular nitrogen valency, and secondly, that the directions of the valencies carrying the acid ions are such that they cannot become identical by the free rotation of the nitrogen atom.

The two salts actually isolated from the products of the neutralisation of the acid and the base both contain externally compensated hydrindamine; consequently, they are composite in character, and each may be regarded as a mixture of two of the above four isomerides; further, as a salt composed of D and D<sub>1</sub> or of L and L<sub>1</sub> would contain optically active base, the isomerides may be regarded as consisting of DL and D<sub>1</sub>L<sub>1</sub>, or of D<sub>1</sub>L and DL<sub>1</sub> respectively.

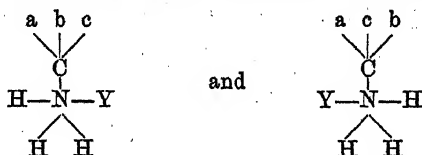
This view, that each salt is made up of two enantiomorphous components which are not enantiomorphously related, and which nevertheless are not separable by fractional crystallisation within certain limits of temperature, might have been considered to be highly improbable, were it not for the existence of partially racemic salts, with which such isomerides as the above are in many ways comparable; there only remains therefore for consideration the important question as to how far the explanation here suggested accords with the facts observed in the study of these isomerides.

This accordance is satisfactory; taking the most important facts in order, the formation of unequal quantities of the two isomerides may first be dealt with.

On examining the formulæ already given, it will be seen that the isomerides D and D<sub>1</sub> should be produced in unequal quantities in the presence of the asymmetry of the hydrindamine molecule; for the

same reason, this is true of the forms L and  $L_1$ . Now if the group X were not enantiomorphous, the two forms D and L would probably be enantiomorphously related, as would also the forms  $D_1$  and  $L_1$ ; consequently, the formation of equal quantities of D and L would be expected, and so also of  $D_1$  and  $L_1$ . The fact that, in the case under consideration, the group X is enantiomorphous, would not apparently condition the formation of unequal quantities of D and L, and the relation between these forms being closer than that between D and  $L_1$ , they might unite to form one of the isomeric salts, the union of  $D_1$  and  $L_1$  producing the other; the two partially racemic salts would thus be formed in unequal quantities.

These arguments may seem somewhat speculative, merely because they are applied to nitrogen, whereas had they been used in the case of carbon they might have been accepted without question; the essential difference between the two cases lies in the fact that with nitrogen it is not possible to say whether the two forms



stand in the relation of object and mirror image when Y represents any non-enantiomorphous group; if they do so, the analogy with carbon is essentially complete.

The fact that the isomerides derived from the sulphonic acids retain their individuality in aqueous and other solvents seems also to be in accordance with the suggested view of their nature.

On referring again to the formulæ on p. 868, it will be seen that hydrolytic dissociation might bring about the partial transformation of one salt into the other; for if D, for example, were to be resolved into acid and base, recombination might give  $D_1$  as well as D; similarly, L might be partially converted into  $L_1$ ; thus the partially racemic salt DL might be changed partly or completely into  $D_1L_1$ , or *vice versa*, by dissolving in water and then evaporating.

So far as can be ascertained, the isomeric salts of the sulphonic acids do not undergo hydrolytic dissociation to an appreciable extent, and in accordance with this conclusion these salts are not convertible one into the other by solution in water. The *cis*- $\pi$ -camphanates, however, do undergo hydrolytic dissociation, and experiment shows that they are also slowly converted one into the other in aqueous solution.

As regards electrolytic dissociation, the case is altogether different, since to whatever extent this change may occur, it would seem that each of the four forms, D,  $D_1$ , L, and  $L_1$ , should be regenerated

unchanged by the recombination of its ions ; in this respect, therefore, the facts are again in agreement with the explanation which has been put forward.

The fact that the base regenerated from one of the salts yields both isomerides on recombination with the acid would be a necessary consequence of the above explanation, and need not be discussed.

The partial conversion of the one isomeride into the other by treating it with an aqueous solution of the externally compensated base is also a consequence of this explanation ; in aqueous solution, the given salt undergoes ionic dissociation, and, on concentrating again, the acid ions unite, not only with the base ions of the original salt, but also with those of the added base ; all the four isomerides, D, D<sub>1</sub>, L, and L<sub>1</sub>, will thus be formed, a condition of equilibrium will be attained, and, on evaporating, the two salts will result. If also the more readily soluble isomeride be repeatedly evaporated with small quantities of externally compensated base, it will be finally almost completely transformed into the more sparingly soluble  $\alpha$ -salt, as is found to be the case.

With reference to the optical behaviour of these isomerides, it is not easy to decide whether their properties are or are not in accordance with the above view of their isomerism ; an inspection of the formulæ on p. 868 will show that when the salts undergo ionic dissociation, the forms D and L give rise to base ions which are either enantiomorphously related or else only partially so, according to the configuration of the nitrogen atom ; this is true also of the base ions of D<sub>1</sub> and L<sub>1</sub>. In the first case, the molecular rotations of the  $\alpha$ - and  $\beta$ -salts should be identical and equal to that of the contained acid ; in the second case, they would probably not be identical, but their mean should be the molecular rotation of the acid ; it is assumed, of course, that the solutions are sufficiently dilute to give the rotations of the ions only.

As a matter of fact, the molecular rotations of all the isomerides, with the exception of the  $\beta$ -salt of the bromo-acid, are practically the same as those of the acid which they contain, and no satisfactory explanation of this exception is forthcoming, unless it be assumed that dissociation is far too incomplete to allow of a normal result being obtained ; several objections to such an assumption might, of course, be advanced, but there are still so many facts in connection with optical activity which require explanation, that the apparently abnormal behaviour of the  $\beta$ -bromo-salt may for the present be passed over.

Much more extraordinary is the behaviour of the  $\alpha$ -salt of *cis*- $\pi$ -acid ; this isomeride, as already stated, shows a marked  $\beta$ -rotation in certain cases, and its specific rotation in methyl

alcoholic solution of a fixed concentration varies within very wide limits; in the case of both isomerides, *different samples of one and the same salt, having the same melting point, have been found to differ greatly in specific rotation when examined in solutions of the same concentration in 99.8 per cent. methyl alcohol.* So far these facts, which are apparently unique, remain unaccounted for; it is not impossible that a partial separation of the D and L components by repeated crystallisation may have occurred in such cases, but there is no direct evidence at present that any such change has taken place.

Having now dealt with the more important experimental data in relation to the explanation which has been suggested to account for the formation and properties of these isomeric salts, it will be manifest that much still remains to be done before any definite conclusion can be arrived at as to the validity of the view which has been advanced; with this object, various investigations have already been commenced, and it is hoped that other instances of such partially racemic isomeric salts may soon be described. There is, however, one very obvious objection which might be raised to the view in question—namely, that if it be adopted, all nitrogen bases, whether optically active or not, should give rise to two salts on combination with an acid or with an alkyl iodide; this objection may be briefly considered.

Dealing in the first place with optically inactive bases and acids, if it be assumed that the two nitrogen valencies concerned in salt formation be symmetrically situated with respect to the other three, the two isomeric salts would be enantiomorphously related, and would not, therefore, be separable by crystallisation if they showed the ordinary behaviour of such isomerides; they would, of course, be formed in equal quantities.

If, however, the base, or the acid, were enantiomorphous, unequal quantities of non-enantiomorphously related isomerides would probably be produced; the question then arises, Would such isomerides be separable by fractional crystallisation? because, if so, it might be concluded that their formation would have been observed long before now. Bearing in mind the existence of partially racemic salts, it seems very probable that such isomerides would not be separable by the ordinary methods; even if they were, it would probably be with great difficulty. Since, moreover, hydrolytic dissociation might bring about the conversion of one form into the other, it is probable that in the great majority of cases it would be impossible to isolate the more readily soluble modification, except with the aid of non-hydrolytic solvents. Since, finally, one of the isomerides may be produced in comparatively very small quantities, it might easily escape detection; many instances, drawn from cases of ordinary isomerism, might be quoted in support of this statement, but it is unnecessary to do so.

Dealing next with the salt produced by the combination of an enantiomorphous base with an enantiomorphous acid, it is again possible that such a substance may consist of unequal quantities of two isomerides which are not enantiomorphously related; such isomerides would be similar to the D and D<sub>1</sub> forms discussed above, and with regard to the possibility of separating them, much the same may be said as in the case just considered. Although it might seem probable that such isomerides would differ to a greater extent than when only one of the components (acid or base) is enantiomorphous, the comparatively small number of such salts which have been examined, and their lack of definite characteristics, might be quoted as a possible reason why isomerism of this kind has not yet been observed. It is also conceivable that the two isomerides D and D<sub>1</sub> might be so similar that they could not be separated, and yet that by union with L and L<sub>1</sub> respectively they might give rise to very different partially racemic salts, just as enantiomorphously related substances give rise to ordinary racemic compounds.

Passing, lastly, to the case of externally compensated bases combining with an optically active acid, it is known already that they may behave in three different ways: (1) They may form only one partially racemic salt; (2) they may give two salts, corresponding with the enantiomorphously related bases, which are separable by crystallisation; (3) they may give two isomeric partially racemic salts, such as those described in this paper.

Whether, in these three cases, the original product consists of four, or of only two, isomerides, is a question which has still to be answered, and one which involves considerations regarding the stereochemistry of the nitrogen atom.

## EXPERIMENTAL.

### I. *Isomeric Hydrindamine Bromocamphorsulphonates.*

An aqueous solution of bromocamphorsulphonic acid is neutralised with hydrindamine, partly dissolved and partly suspended in water, and concentrated on the water-bath; on cooling, the solution becomes semi-solid, owing to the separation of a felted, opaque mass of needles; this product is separated by filtration, the mother liquors again concentrated, and allowed to crystallise. These processes having been repeated several times, the last mother liquors give a deposit differing in appearance from previous ones, and on further fractional crystallisation from water or very dilute alcohol, two different products are finally obtained in a state of purity. The intermediate deposits are again fractionally crystallised, but they consist principally of the more

sparingly soluble salt, and only small quantities of the less soluble compound are obtained from them.

*α-Salt.*

The more sparingly soluble salt, which will be subsequently referred to as the  $\alpha$ -salt, usually separates from cold or tepid water in bulky, felted masses of very slender, concentrically-grouped needles, but it is deposited as an oil if the solution be too concentrated and separation occur too quickly. Very occasionally, when evaporation of a nearly saturated solution takes place slowly at the ordinary temperature, the salt separates at, or near, the surface of the liquid in large, transparent, compact, but ill-defined prisms. It dissolves fairly easily in cold methyl or ethyl alcohol, and in hot water, but it is only moderately soluble in cold ethyl acetate and cold water; it crystallises from ethereal alcohol in long, transparent, ill-defined prisms.

The moss-like crystals obtained from aqueous, and the prisms deposited from alcoholic, solution, contain water of crystallisation, and when dried on porous earthenware, and then quickly heated, they usually liquefy partially or completely at about  $100^{\circ}$ ; the compact prisms, more rarely obtained, do not liquefy at  $100^{\circ}$ , but slowly become opaque. On exposure to the air at ordinary temperatures, the crystals effloresce, but so slowly that they continue to lose in weight during many days, and even when dried in the air until constant they still contain water of crystallisation, and liquefy or become pasty when heated at  $100^{\circ}$ . After prolonged drying at  $100^{\circ}$ , the  $\alpha$ -salt shows a constant and fairly definite melting point, namely,  $149-151^{\circ}$ .

Numerous determinations of the water of crystallisation were made, but they did not give very satisfactory results; it would seem that the freshly crystallised salt contains  $1\frac{1}{2}$  mols.  $H_2O$ , whereas the air-dried crystals contain less than  $1\frac{1}{2}$  mols.

One gram of salt from ethereal alcohol, dried over night in the air, lost 0.0669 gram  $H_2O$ .  $H_2O = 6.69$  per cent.

With samples air-dried until constant in weight, the following results were obtained:

0.5 lost 0.0272  $H_2O$  at  $100^{\circ}$  during 72 hours.  $H_2O = 5.44$  per cent.

1.0 „ 0.0509  $H_2O$  „ „ 100 „ „  $H_2O = 5.09$  „

0.5 „ 0.0265  $H_2O$  „ „ 60 „ „  $H_2O = 5.3$  „

$C_{10}H_{14}BrO \cdot SO_3H \cdot C_9H_{11}N + 1\frac{1}{2}H_2O$  requires  $H_2O = 6.62$  per cent.

$C_{10}H_{14}BrO \cdot SO_3H \cdot C_9H_{11}N + 1\frac{1}{2}H_2O$  „ „  $H_2O = 5.7$  „

$C_{10}H_{14}BrO \cdot SO_3H \cdot C_9H_{11}N + 1\frac{1}{2}H_2O$  „ „  $H_2O = 4.82$  „

The disagreement between the observed and the calculated results in the case of the air-dried salt may perhaps be due to the difficulty of

ascertaining when efflorescence has ceased, and to the prolonged heating at  $100^{\circ}$  required to expel the last traces of water; on the other hand, it might be taken as an indication that the salt is not homogeneous.

Bromine determinations in a sample of the salt dried at  $100^{\circ}$  gave the following results:

0.1629 gave 0.0704 AgBr. Br = 18.3 per cent.

0.1449 „ 0.0626 AgBr. Br = 18.4 „

$C_{10}H_{14}BrO \cdot SO_3H \cdot C_9H_{11}N$  requires Br = 18.0 per cent.

The air-dried salt is readily soluble in boiling benzene and very readily soluble in cold chloroform, but it does not seem to crystallise from either solvent, except by gradual absorption of moisture from the air with formation of the ordinary hydrated crystals; on evaporating a benzene or chloroform solution, the salt is deposited as a gum-like mass.

#### *$\beta$ -Salt.*

The more readily soluble hydrindamine bromocamphorsulphonate, which is hereafter referred to as the  $\beta$ -salt, nearly always separates from cold or tepid water in small, compact, fairly well-defined transparent prisms, which often form concentrically grouped masses; the appearance of these crystals is always absolutely different from that of the opaque, felted masses of the  $\alpha$ -salt, but they are not easily distinguished by mere inspection from the compact prisms of the latter which are occasionally obtained. The crystals of the  $\beta$ -salt become opaque but do not liquefy at  $100^{\circ}$ , and they do not effloresce appreciably on exposure to the air; they become opaque when warmed in contact with their saturated aqueous solution. After having been dried at  $100^{\circ}$ , they have a constant and fairly definite melting point, namely,  $129-130^{\circ}$ . The  $\beta$ -salt is more readily soluble in cold water than the  $\alpha$ -compound, and, like the latter, it is deposited as an oil from warm saturated solutions; it dissolves freely in cold alcohol and ethyl acetate.

The air-dried salt contains  $\frac{3}{4}$  mol. of water of crystallisation:

0.5 lost 0.0129  $H_2O$  at  $100^{\circ}$  during 60 hours.  $H_2O = 2.58$ .

1.6612 „ 0.0453  $H_2O$  „ 96 „  $H_2O = 2.72$ .

0.8328 „ 0.0228  $H_2O$  „ 48 „  $H_2O = 2.73$ .

$C_{10}H_{14}BrO \cdot SO_3H \cdot C_9H_{11}N + \frac{3}{4}H_2O$  requires  $H_2O = 2.73$  per cent.

Bromine determinations in the salt dried at  $100^{\circ}$  gave the following results:

0.2000 gave 0.0874 AgBr. Br = 18.5.

0.2072 „ 0.0873 AgBr. Br = 18.0.

$C_{10}H_{14}BrO \cdot SO_3H \cdot C_9H_{11}N$  requires Br = 18.0 per cent.



The air-dried salt is readily soluble in benzene or hot chloroform, but on allowing such solutions to evaporate, it is deposited as a gum which gradually crystallises owing to absorption of water; no particular effort was made to obtain anhydrous crystals either in this case or in that of the  $\alpha$ -salt.

*Molecular Weight Determinations*,  $C_{10}H_{14}BrO \cdot SO_3H, C_9H_{11}N = 444$ .

Molecular weight determinations were made by the cryoscopic method in dilute aqueous solution; the results show that the salts are isomeric and that both are largely dissociated.

*$\alpha$ -Salt.*

Weight of solvent.	Weight of substance.	Grams substance in 100 grams solvent.	Depression of freezing point.	M.W.
25 grams	0.2	0.8	0.075	203
25 "	0.2	0.8	0.067	227

Taking the water of crystallisation in the sample as 5.2 per cent., the average result for the anhydrous salt would be M.W. = 204.

*$\beta$ -Salt.*

Weight of solvent.	Weight of substance.	Grams substance in 100 grams solvent.	Depression of freezing point.	M.W.
25 grams	0.3	1.2	0.100	228
25 "	0.2	0.8	0.065	234
25 "	0.3	1.2	0.090	253

The water of crystallisation in the  $\beta$ -salt being 2.7 per cent., the average value for the molecular weight of the anhydrous salt would be 232.

*The Salts do not contain Enantiomorphously Related Bases.*

Having obtained these isomeric salts by the combination of externally compensated hydrindamine with bromocamphorsulphonic acid, it seemed most probable that the former had been resolved into its optically active components. Accordingly, a sample (10 grams) of the pure  $\alpha$ -salt was treated with excess of barium hydroxide, and the liberated base separated by steam distillation; the distillate, after the addition of a little alcohol to dissolve the oily base, occupied about 100 c.c., and a portion of it, on examination in a 200 mm. tube, was found to give no appreciable rotation.

Of course, this result did not prove that a resolution of the externally compensated base had not occurred, as the specific rotation of its

optically active components might have been too small to detect except in a very concentrated solution, and with a very sensitive polarimeter; or the specific rotation might even be *nil* in spite of the base being an optically active compound. So, in order to ascertain whether this was or was not the case, a portion of the base which had been regenerated from the  $\alpha$ -salt was converted into its hydrochloride; the latter melted at the same temperature as the hydrochloride of the externally compensated base, and was identical with the latter in all ordinary properties. Another portion of the regenerated base was converted into its benzoyl derivative by the Schotten-Baumann method; the product, after recrystallisation, was identical in melting point and appearance with the benzoyl derivative of ordinary hydrindamine (Reis and Kipping, *Trans.*, 1897, 71, 251), and a small quantity of it, examined optically in benzene solution, gave no appreciable rotation.

These observations seemed to prove that the base regenerated from the  $\alpha$ -salt was really an externally compensated compound, identical with the base obtained directly from hydrindoxime, but the evidence was not absolutely conclusive. Both the hydrochloride and the benzoyl derivative of the externally compensated base might possibly be mere mixtures, and not racemic substances, and by a further possibility, the melting points of these compounds might be practically identical respectively with those of the optically active hydrochloride and benzoyl derivative. As, moreover, it is very difficult to make sure that the  $\alpha$ -salt is perfectly free from the more sparingly soluble  $\beta$ -salt, owing to the ill-defined character of its crystals, and the sample used might conceivably have contained a little of the  $\beta$ -salt even after repeated crystallisation, it seemed necessary to examine the latter, as being a much better characterised substance.

A carefully purified sample (4 grams) of the  $\beta$ -salt was, therefore, decomposed as described in the case of the  $\alpha$ -compound. The aqueous alcoholic solution of the regenerated base, which measured less than 50 c.c., produced no appreciable rotation in a 200 mm. tube, and the base was found to be identical in every respect with that obtained from the  $\alpha$ -salt.

In spite of the apparently conclusive results of these experiments, it seemed advisable to apply a crucial test, namely, to ascertain whether the base of the one salt would differ from that of the other, if combined with an optically active substance. For this purpose, samples of the two bases were separately treated with *d*-camphoric acid; the salts thus obtained were identical in melting point and in ordinary properties. Similar experiments were made, using *cis*- $\pi$ -camphanic acid (p. 903) as the optically active substance; again, the base from the  $\alpha$ -salt gave the same product as that obtained with the base from the  $\beta$ -salt.

These facts prove that the bases regenerated from the two salts are not enantiomorphous, and that their optical inactivity is not merely a fortuitous instance of very low specific rotatory power.

*Relative Quantities of the Two Isomerides.*

Another fact which accords with this conclusion is, that the two isomeric salts are not obtained in even approximately equal quantities. After repeated fractional crystallisation of the original mixtures, carried as far as possible, with the object of ascertaining roughly the relative proportions of the isomerides, there is always obtained at least four times as much of the  $\alpha$ - as of the  $\beta$ -salt.

*The Salts are not merely Different Crystalline Varieties.*

The formation of the two isomerides could hardly be attributed to a difference in the degree of hydration of their crystals, as they are both deposited from water at the ordinary temperature, apparently under the same conditions; moreover, the (completely dehydrated) salts have different melting points and different specific rotatory powers.

Dimorphism is also out of the question for similar reasons, and it may be explicitly stated that, although the two salts have been crystallised over and over again during the time they have been under investigation, the partial conversion of one into the other has never been observed except under the particular conditions described later (p. 882). It must again be noted, however, to avoid misunderstanding, that very occasionally, under conditions not precisely ascertained, the  $\alpha$ -salt crystallises from cold water in compact prisms, difficult to distinguish from those of the  $\beta$ -salt by mere inspection, but which have nevertheless the melting point and other specific properties of the  $\alpha$ -salt.

*Examination of the Acid contained in the Salts.*

The possibility that the bromocamphorsulphonic acid might be the cause of the formation of the two salts may next be considered. The acid used in these experiments was prepared from purified ammonium bromocamphorsulphonate (Kipping and Pope, *Trans.*, 1895, 67, 358), and although in the course of work with this acid and its derivatives no indication of the presence of any isomeride had ever been observed, it was desirable to obtain experimental proof that the acid of the  $\alpha$ -salt is really identical with that of the  $\beta$ -isomeride.

As the latter is formed in much the smaller quantity, it would be in this compound, if anywhere, that the isomeric acid would be found. The pure  $\beta$ -salt was therefore decomposed with barium

hydroxide, the base separated, the barium salt converted into ammonium salt, and the latter isolated; it was identical with ordinary ammonium bromocamphorsulphonate in all outward properties, and had the same specific rotatory power as the latter. Further, when triturated with phosphorus pentabromide, it gave a sulphonic bromide identical with the compound obtained from ordinary ammonium bromocamphorsulphonate.

*The Base from one Salt gives both Isomerides when combined with the Acid.*

The next experiments which were made had the object of ascertaining whether the base regenerated from one of the salts would, or would not, give the same salt when neutralised again with bromocamphorsulphonic acid.

A sample of the  $\alpha$ -salt, which had the correct melting point, was first carefully fractionally crystallised from water, and it was proved that the last mother liquors did not deposit even traces of the more readily soluble  $\beta$ -salt. A quantity of the same sample was then decomposed with barium hydroxide, the base distilled in steam, and the distillate neutralised with bromocamphorsulphonic acid; on then submitting the product to fractional crystallisation from water, the first and several subsequent deposits were found to be the  $\alpha$ -salt, but the last mother liquors deposited crystals of the  $\beta$ -salt, and, as far as could be judged, the proportion of the two isomerides was just about the same as that in which they are formed from the ordinary externally compensated base.

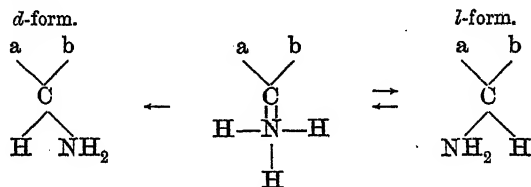
The  $\beta$ -salt was then treated in a similar manner; on fractional crystallisation from water, it afforded no indication of the presence of the isomeride, but when decomposed with barium hydroxide it yielded a base from which, on neutralising with bromocamphorsulphonic acid and fractionally crystallising, both the  $\alpha$ - and  $\beta$ -salts were obtained; in this case, again, the relative weights of the two salts seemed to be just about the same as usual.

*The Free Base does not undergo Racemisation.*

These last experiments, and many other facts already recorded, might be explained by assuming that the base is actually resolved into its enantiomorphously related components when its salt with bromocamphorsulphonic acid is fractionally crystallised, but that when liberated from its salt, or during steam distillation, the optically active substance racemises.

Although the mechanism of racemisation is not yet capable of satisfactory explanation, it is conceivable that, in the case of a primary

base such as hydrindamine, this change might be brought about as the result of the existence of tautomeric modifications, which might cause a transformation of one enantiomorphous form into the other in the following manner :



These changes do not require further explanation, and it will be seen that the possibility of racemisation would depend here upon the direct union of the amino-group with the asymmetric carbon group ; it seems not unlikely that changes such as these actually occur in the racemisation of  $\beta$ -aspartic acid, for example, and in the case of other optically active amino-compounds of this class, many of which are converted into the inactive modifications comparatively easily.

Considering, now, whether this assumption of the occurrence of racemisation would explain the existence of the isomeric salts, one very important objection immediately suggests itself, namely, the fact that the two compounds are formed in such very unequal quantities when the base is neutralised with the acid. Although it has been recently shown by Marckwald and McKenzie (*Ber.*, 1899, 32, 2130) that in the combination of the enantiomorphously related mandelic acids with menthol, the two antipodes have a different reaction velocity, and after a certain period of interaction give a product consisting of unequal quantities of the two menthyl mandelates, the difference is only very small, and it is extremely unlikely that any analogous difference in the case of the combination of the two enantiomorphous hydrindamines with bromocamphorsulphonic acid could lead to the production of such unequal quantities of their salts, even if at the same time the free base were undergoing rapid autoracemisation. These remarks apply, of course, only if hydrolytic dissociation be excluded ; if, however, hydrolytic dissociation were to accompany autoracemisation, one of the salts should be partially or completely converted into the other on recrystallisation from water.

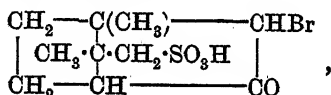
The experimental evidence which can be advanced against the view that optically active hydrindamine may undergo autoracemisation is not of much weight in the case of the two bromocamphorsulphonates, and merely amounts to this : that on decomposing either the  $\alpha$ - or the  $\beta$ -salt with barium hydroxide in cold aqueous solution, and then quickly extracting the base with ether, the ethereal solution is found to show no appreciable optical activity. This experiment merely

proves that if autoracemisation takes place at all, it must occur with great rapidity, even at low temperatures, a conclusion which can hardly be regarded with favour. But the arguments just advanced, the optical behaviour of the two salts, and further experimental evidence which will be brought forward later, show conclusively that an explanation of the isomerism of the two salts, based on the assumption of autoracemisation, is quite out of the question.

*The Isomeric Salts are derived from one and the same Acid.*

If autoracemisation of the base be excluded, and the  $\alpha$ - and  $\beta$ -salts contain one and the same externally compensated hydrindamine, it might be concluded that the acid must be the cause of the isomerism. This possibility has already been considered superficially, and it has been shown that the acid obtained, after a series of operations, from the  $\beta$ -salt is identical with ordinary bromocamphorsulphonic acid (p. 877).

An inspection of the following formula,



which has previously been assigned to  $\alpha$ -bromocamphorsulphonic acid (Kipping, Trans., 1896, 69, 913), will, however, make it obvious that there are certain ways in which this acid might possibly give rise to two salts, and yet appear to be a single individual. For reasons which will be evident when the molecular rotations of the hydrindamine salts have been dealt with, it seemed at one time very probable that the acid of the  $\beta$ -salt was really different, in some way, from that of the  $\alpha$ -isomeride; it was consequently necessary to make a number of experiments, in order to exclude this possibility.

The existence of desmotropic forms of the acid, namely, a ketonic  $\cdot\text{CHBr}\cdot\text{CO}\cdot$  and an enolic  $\cdot\text{CBr}\cdot\text{C}(\text{OH})\cdot$ , is perhaps the simplest of the possible explanations which might suggest itself, as the  $\alpha$ -salt might be regarded as derived from one, the  $\beta$ -salt from the other modification.

Such a view does not seem to commend itself for many reasons, and firstly on theoretical grounds, since, so far as is known, camphor itself, and its simple substitution derivatives which contain the group  $\cdot\text{CHX}\cdot\text{CO}\cdot$ , do not exhibit the phenomenon of desmotropism.

The experimental evidence which can be brought forward against this view also seems to be conclusive. If the supposed desmotropic acids were so stable that aqueous solutions of their hydrindamine salts might be boiled without converting the one into the other, it seems

most unlikely that mere displacement of the hydrindamine by barium and ammonium successively in hot aqueous solution would bring about such a change, and yet the ammonium bromocamphorsulphonate prepared from the  $\beta$ -salt by the usual method is identical with ordinary ammonium bromocamphorsulphonate (p. 877).

It can also be proved that when this displacement occurs at temperatures below  $20^{\circ}$  the result is the same:—A sample of the  $\beta$ -salt was treated with a large excess of concentrated ammonia in the cold, and the liberated organic base extracted with ether; the aqueous solution of the ammonium salt was then evaporated almost to dryness at the ordinary temperature, concentrated ammonia added, and the solution again repeatedly extracted with ether. After evaporating at the ordinary temperature, the ammonium bromocamphorsulphonate was obtained in crystals, which were identical with those of the ordinary ammonium salt in outward and in optical properties.

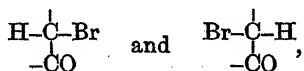
Now, as a general rule, desmotropic forms are easily converted one into the other by a change of temperature, or with the aid of a trace of piperidine (Schiff, *Ber.*, 1898, 31, 601) or of sodium ethoxide. Accordingly, attempts were made to convert the  $\alpha$ - into the  $\beta$ -salt and *vice versa*, but without success, and it was thus found that the two isomerides do not show the ordinary behaviour of desmotropic forms in any way whatever.

The salts, as already stated, are not changed when they are repeatedly crystallised from water or other solvents, nor when heated to fusion in their water of crystallisation. Ferric chloride, so reliable a reagent in most cases for the detection of the enolic modification, gives no coloration with either the  $\alpha$ - or the  $\beta$ -salt in aqueous or in alcoholic solutions.

Neither of the salts interacts with phenyl isocyanate; samples of each, dried at  $100^{\circ}$ , were left in contact with this reagent during several days, but neither underwent any change; portions which had been treated in this way, and then merely washed with ether on porous earthenware, showed the melting points of  $130^{\circ}$  and  $150^{\circ}$  respectively, and after dissolving in water and filtering from diphenyl-carbamide, the solutions, on evaporation, gave the  $\alpha$ - and  $\beta$ -salts respectively in an unchanged condition. Had either of the salts been derived from an enolic form of bromocamphorsulphonic acid, it is probable that it would have interacted with the phenyl isocyanate.

Samples of the dehydrated salts were also separately recrystallised from benzene in presence of traces of piperidine; no change, however, was brought about in either case, and after recrystallisation from water (an operation which is known to have no effect on either salt), the two compounds still had their original properties, and were apparently quite free from isomeride.

The only other manner, apparently, in which the bromocamphor-sulphonic acid might be accountable for the formation of two hydrindamine salts, would be the existence of two stereoisomeric forms represented by the formulæ



but it will be obvious that such an assumption is quite untenable for many reasons which it is unnecessary to specify.

It has thus been shown that the isomeric hydrindamine bromocamphorsulphonates are derived from one acid only, and that their isomerism is in no way referable to the existence of physically or chemically different forms of this acid; this conclusion does not rest merely on the experimental evidence recorded in this paper, but is supported by such an array of facts, which cannot conveniently be discussed here, that it may be regarded as final.

#### *Conversion of the $\beta$ - into the $\alpha$ -Salt.*

Although all attempts to convert one of the hydrindamine salts into the isomeride by crystallisation, or by dissolution in and evaporation with solvents, were unsuccessful, it was found that the  $\beta$ -salt could be almost entirely transformed into the isomeride by repeatedly evaporating its aqueous solution with externally compensated hydrindamine; the operation is so simple that further description is unnecessary.

In a similar manner, the  $\alpha$ -salt may be partly converted into the  $\beta$ -isomeride.

That in this process hydrolytic dissociation plays no part is proved by the fact that in absence of added base, the change does not occur; it can also be shown in other ways that the salts do not undergo hydrolytic dissociation to any appreciable extent. The conversion of one isomeride into the other under the conditions just stated is therefore a process essentially different from that in which this partial transformation is brought about by first liberating the base, and then treating again with fresh bromocamphorsulphonic acid (p. 878).

Two diametrically opposite views might be held as to the interpretation of the fact just recorded. On the one hand, it might be considered as conclusive evidence that the  $\alpha$ - and  $\beta$ -salts are not derived from physically or chemically isomeric acids; since base alone is added during the transformation. On the other hand, it might be assumed that the presence of free base causes a change to take place in the physical or chemical character of the acid; if the presence of a trace of piperidine may bring about the conversion of an enolic form



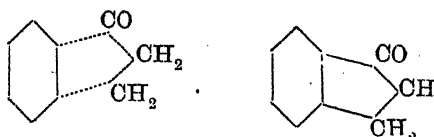
into the ketonic isomeride, the free base, hydrindamine, might play a similar part. The possibility of the latter view being adopted made it necessary to show by the experiments already recorded that bromocamphorsulphonic acid exists only in the one form.

*Hydrindamine is composed of Two Enantiomorphous Modifications only.*

Another very natural conclusion which might be drawn from the fact that the  $\beta$ -salt is converted into the  $\alpha$ -isomeride on evaporation with fresh quantities of the externally compensated base would be, perhaps, that the hydrindamine supplied to the acid during this process is different, partly or entirely, from the base to which the acid is already united.

To conclude that one enantiomorphous base displaces the other would, of course, necessitate the further assumption that the two isomeric salts correspond in the ordinary manner with the two enantiomorphously related bases, a view which has already been discussed and shown to be untenable.

The question as to whether the base exists in two modifications which are not enantiomorphously related has not yet been raised, and, in fact, it is hardly necessary to consider it. If the hydrindene and benzene chains did not lie in one plane, there might, of course, be two stereoisomeric hydrindones, as represented roughly by the following formulæ:



and each of these would give rise to two different optically active bases. There would thus be two different externally compensated hydrindamines, which would be related to one another in much the same way as optically inactive bornylamine and neobornylamine, for example; the two externally compensated compounds would then be different altogether, and would necessarily give different salts and other derivatives, just as do the optically active bornylamines (Forster, *Trans.*, 1898, 73, 386).

As it has already been shown that the base of the  $\alpha$ -salt is identical, chemically and physically, with that of the  $\beta$ -isomeride, the possible existence of isomeric inactive hydrindamines need not be further discussed.

The results of the experiments which have now been described may be briefly summarised as follows: Externally compensated hydrindamine, which is a mixture of two enantiomorphously related forms,

combines with *d*-bromocamphorsulphonic acid, giving unequal quantities of two isomeric salts. The base and the acid of which one salt is composed are identical respectively, both physically and chemically, with the components of its isomeride.

## II. *Specific and Molecular Rotations of the Hydrindamine Bromocamphorsulphonates.*

The optical examination of the  $\alpha$ - and  $\beta$ -salts described in the preceding section shows that the isomerides have different specific rotations in methyl alcohol, chloroform, and aqueous solutions, that of the  $\alpha$ -compound being in all cases considerably higher than that of the isomeride.

*Methyl Alcohol Solutions.*—The samples were dried at 100° until practically constant in weight; 1 gram of each was then separately dissolved in 99 per cent. methyl alcohol, the solution diluted to 25 c.c., and examined in a 200 mm. tube at about 16°.

$\alpha$ -Salt	.....	$\alpha + 5^{\circ} 19'$	$[\alpha]_D + 66.6^{\circ}$	$[M]_D + 296$
$\beta$ -Salt	.....	$\alpha \quad 4^{\circ} 25'$	$[\alpha]_D \quad 55.2$	$[M]_D \quad 245$

Optical examination was next made in more dilute solutions, 0.5 gram being used, the samples of salt, solvent, and all other conditions being the same as before.

$\alpha$ -Salt	.....	$\alpha + 2^{\circ} 36'$	$[\alpha]_D + 65.0^{\circ}$	$[M]_D + 289$
$\beta$ -Salt	.....	$\alpha \quad 2^{\circ} 12'$	$[\alpha]_D \quad 55.0^{\circ}$	$[M]_D \quad 244$

These values show that the change in concentration from about 4 to 2 per cent. produces no appreciable effect on the specific rotation.

*Chloroform Solutions.*— $\alpha$ -Salt: 0.5 gram of the anhydrous salt was dissolved in, and made up to 25 c.c. with chloroform, the solution being examined in a 200 mm. tube.  $\beta$ -Salt: 0.5 gram of air-dried salt containing 2.7 per cent. of water was treated in the same way: the molecular rotation is calculated for the anhydrous compound.

$\alpha$ -Salt	.....	$\alpha + 1^{\circ} 53'$	$[\alpha]_D + 47.3^{\circ}$	$[M]_D + 210$
$\beta$ -Salt	.....	$\alpha \quad 1^{\circ} 40'$	$[\alpha]_D \quad 41.5^{\circ}$	$[M]_D \quad 190$

### *Aqueous Solutions.*

Observations were next made in dilute aqueous solutions: 0.25 gram of each of the dehydrated salts was dissolved, the solution made up to 25 c.c., and examined in a 200 mm. tube at about 16°.

$\alpha$ -Salt	.....	$\alpha + 1^{\circ} 10'$	$[\alpha]_D + 58.3^{\circ}$	$[M]_D + 259$
$\beta$ -Salt	.....	$\alpha \quad 0^{\circ} 58'$	$[\alpha]_D \quad 48.3^{\circ}$	$[M]_D \quad 214$

Now the molecular rotation,  $[M]_D$ , of bromocamphorsulphonic acid in aqueous solution is +270, and it might therefore be inferred from these results that the base of the  $\beta$ -salt is levorotatory, whilst that of the  $\alpha$ -compound is either very feebly levorotatory or optically inactive; but, in view of the rather large experimental error which is unavoidable in dealing with such dilute solutions, it was necessary to make further determinations with different samples of the two salts before much weight could be attached to the results.

In the first of this new series of experiments, the samples were again dried at 100° until constant in weight, an operation which lasted during many hours; the following results were then obtained, the samples marked with an asterisk being different from the other two; a 200 mm. tube was used in all cases.

 *$\alpha$ -Salt.*

Weight of substance.	Volume of solution.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
0.9331	25 c.c.	+4°43'	+63.1°	+280
0.2333	"	1°8'	60.5	268
*0.4735	"	2°31'	60.7	270

 *$\beta$ -Salt.*

0.8100	25 c.c.	+3°31'	+54.3°	+241
0.2025	"	0°52'	53.5	237
*0.4862	"	2°6'	54.0	240

These results confirm those previously obtained in the case of the  $\alpha$ -salt within the limits of experimental error, but in the case of the  $\beta$ -salt, the values of the molecular rotation are about 10 per cent. higher than that previously found. As it seemed possible that this disagreement might be the result of such prolonged heating at 100°, fresh determinations were made with air-dried samples of the two salts, and the combined water was determined in other portions of the same samples; the following results were thus obtained, using water as solvent and a 200 mm. tube.

The specific and molecular rotations are calculated for the anhydrous salts.

 *$\alpha$ -Salt.*

Weight of substance.	Volume of solution.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
0.2500	25 c.c.	+1°8'	+59.7°	+265
0.5000	"	2°17'	60.3	268

The sample of the  $\alpha$ -salt contained 5.3 per cent. of water.

*$\beta$ -Salt.*

Weight of substance.	Volume of solution.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
0.2500	25 c.c.	+0°59'	+50.3°	+223
0.5000	"	1°54'	49.0	218

The sample of the  $\beta$ -salt contained 2.76 per cent. of water.

The samples marked above with an asterisk were the same respectively as those used in the last experiments, but the marked samples were dehydrated before the specific rotations were determined; it would seem, therefore, that prolonged heating at 100° raises the specific rotation of the  $\beta$ -salt to a very slight extent, but has no effect on that of the  $\alpha$ -salt. If such a change really does occur, it does not consist in the conversion of the  $\beta$ - into the  $\alpha$ -isomeride, because on evaporating an aqueous solution of a sample of the  $\beta$ -salt which has been heated during several days at 100°, the crystalline deposit does not show the presence of even traces of the  $\alpha$ -compound.

Accepting the values for the molecular rotations obtained in the last series of experiments, which are probably the most trustworthy, and assuming that they are practically the same as those of the fully dissociated salts, it might be provisionally assumed that the base ion of the  $\alpha$ -salt is optically inactive, whereas that of the  $\beta$ -salt shows a molecular rotation of about  $-50^\circ$ .

At this stage of the investigation, for reasons which will be obvious, it seemed desirable to ascertain whether the value obtained for the molecular rotation of bromocamphorsulphonic acid in the case of salts analogous to the hydrindamine compounds would correspond with that deduced from an examination of its metallic salts; ammonium bromocamphorsulphonate and aniline bromocamphorsulphonate were therefore examined in 1 to 4 per cent. aqueous solutions with the following results:

*Ammonium bromocamphorsulphonate.*

Weight of salt.	Volume of solution.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
1 gram	25 c.c.	+6°47'	+84.8°	+278
0.5 "	"	3°24'	84.8°	278
0.25 "	"	1°40'	83.5°	274

*Aniline bromocamphorsulphonate.*

Weight of salt.	Volume of solution.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
0.5 gram	25 c.c.	+2°39'	+66.3	+268
0.25 "	"	1°20'	67.0	271

These results are practically identical with those obtained by *Wiedemann (loc. cit.)* and therefore do not afford any good reason for reject-

ing the provisional assumption just made, namely, that the molecular rotation of the  $\alpha$ -salt is normal on the supposition that the base is optically inactive, whereas that of the  $\beta$ -salt indicates the presence of lævorotatory hydrindamine.

But it has already been shown that the  $\beta$ -salt must be regarded as partially racemic because the base contained in it is identical with ordinary hydrindamine; further, it cannot be assumed that the  $\beta$ -salt contains lævorotatory base without also assuming that the  $\alpha$ -salt contains the dextrorotatory isomeride, in which case the molecular rotation of the  $\alpha$ -salt could hardly be  $[M]_D = +268$ . Even the assumption that optically active hydrindamine undergoes almost instantaneous racemisation would not account for the existence of a ( $\beta$ )-salt containing lævorotatory base and a more sparingly soluble ( $\alpha$ )-salt containing optically inactive hydrindamine. For these reasons, the abnormal molecular rotation of the  $\beta$ -salt cannot be explained in this simple way.

The existence in the  $\beta$ -salt of an isomeric bromocamphorsulphonic acid, which in the ionic state has a molecular rotation  $[M]_D +220$  is another explanation which might suggest itself, and it was for this reason that it was so necessary to prove by the experiments already recorded that the molecular rotation of the acid of the  $\beta$ -salt is identical with that of ordinary bromocamphorsulphonic acid.

The assumption that the abnormal molecular rotation of the  $\beta$ -salt is due to hydrolytic dissociation might also be made, but even if it were in itself sufficient, it would be in direct conflict with the experimental evidence; so far as can be inferred from the fact that aqueous solutions of the  $\beta$ -salt do not acquire an acid reaction on prolonged boiling, the salt does not undergo hydrolytic dissociation to any appreciable extent; moreover, even in the case of a salt such as morphine bromocamphorsulphonate, which is a salt of a comparatively feeble base, the normal molecular rotation is obtained in dilute aqueous solution (Walden, *Zeit. physikal. Chem.*, 1894, 15, 206).

The last explanation which may be considered is the possibility that the  $\beta$ -salt does not undergo ionic dissociation in 1 per cent. aqueous solution to a sufficient extent to give the normal molecular rotation of its acid ion.

Now Walden has shown that even in very dilute aqueous solutions the metallic salts of bromocamphorsulphonic acid are only dissociated to the extent of 80—90 per cent.; he also found that the extent of dissociation, for solutions of equivalent concentration, varies with the nature of the solvent, being, for example, only about 80 per cent. in the case of the barium salt, but reaching 90 per cent. in the case of the potassium salt, these being the results of determinations in the most dilute solutions which he examined.

As it is very improbable that the salts of hydrindamine with bromocamphorsulphonic acid would be more highly dissociated than the potassium salt of this acid, it may be safely concluded that the former are only partially ionised even in the most dilute solutions (1 per cent.) which were examined, more especially as even these solutions contained about three times as many equivalents of the salt as the most dilute solutions of potassium bromocamphorsulphonate investigated by Walden.

Now, in the case of the metallic salts of bromocamphorsulphonic acid, the molecular rotations vary very little with the extent of dissociation, a difference of about 20 per cent. in the latter making a difference of only 1 or 2 per cent. in the former; it might be thought, therefore, that the value obtained for the molecular rotation of the  $\beta$ -salt in 1 per cent. solution, in which dissociation is probably far from complete, might nevertheless be almost identical with the value which would be obtained in infinitely dilute solution.

This, however, is not a necessary consequence by any means. The  $\beta$ -salt differs profoundly from the metallic salts of bromocamphorsulphonic acid, inasmuch as it contains enantiomorphous base ions, and the union of the latter with the acid ions may give salt molecules which have a molecular rotation widely different from that of the algebraic sum of the molecular rotations of the ions; consequently a small difference in the extent of the dissociation might make a very considerable difference in the observed molecular rotation.

If, then, it could be shown that the specific rotation of the  $\beta$ -salt increased as the concentration of the aqueous solutions diminished, the whole difficulty would be overcome. Unfortunately, however, the solubility of the salt in cold water is so small that solutions containing more than about 2 per cent. cannot be examined, and with those containing less than 1 per cent. the experimental error would be too large; for these reasons, it was impossible to trace the influence of concentration by employing aqueous solutions only.

As the addition of hydrindamine for the purpose of diminishing the ionic dissociation would have been inadmissible, since the free base brings about the partial conversion of one isomeride into the other, and as its salts might do so likewise, this method was also excluded.

Experiments were therefore made in aqueous methyl alcoholic solution as follows: 2 grams of  $\beta$ -salt, containing 2.7 per cent. of water, were dissolved in water containing just sufficient methyl alcohol to prevent crystallisation on diluting with water to 25 c.c.; this solution was examined in a 100 mm. tube.

$$\alpha + 4.98^\circ$$

$$[\alpha]_D + 53.1^\circ$$

$$[M]_D + 236.$$

0.635 grams of the same sample were dissolved in 99 per cent. methyl

alcohol, the solution diluted to 25 c.c., and examined in a 200 mm. tube :

$$\alpha + 10^{\circ}25' \quad [\alpha]_D + 54.2^{\circ} \quad [M]_D + 241$$

The specific and molecular rotations are calculated for the anhydrous salt in both cases.

Since the specific rotation of the  $\beta$ -salt is about  $[\alpha]_D + 55^{\circ}$  in a 2 per cent. solution in methyl alcohol, and about  $+50^{\circ}$  in 1 per cent. aqueous solution, the results of these experiments afford no indication as to whether the specific rotation increases or decreases as concentration diminishes ; from experiments made with aqueous solutions containing about 0.4 per cent. of salt, it would seem that the latter is true, but the experimental error was too large to admit of any positive conclusion being drawn.

The results of the optical examination of this pair of isomerides, taken as a whole, cannot, therefore, be regarded as strictly in accordance with the view that the  $\beta$ -salt is partially racemic, although they confirm this conclusion as regards the  $\alpha$ -salt. On the other hand, the view that the  $\beta$ -isomeride is a salt of levorotatory hydrindamine is so beset with improbabilities that it could not be maintained ; in addition to the reasons already stated against it, there is the obvious relation between the  $\beta$ -salts of the bromo- and chloro-acids, which practically settles the matter, since the value for the molecular rotation of the  $\beta$ -chloro-salt is approximately normal on the assumption that it is partially racemic.

### III. *Isomeric Hydrindamine Chlorocamphorsulphonates.*

The interesting case of isomerism observed in the study of the hydrindamine bromocamphorsulphonates led naturally to the examination of other salts of the externally compensated base, and the close relationship between the sulphonic acids of bromo- and chloro-camphor (Kipping and Pope, *Trans.*, 1893, 63, 548) seemed to justify the conclusion that the hydrindamine salts of chlorocamphorsulphonic acid would be obtainable in isomeric forms, corresponding with those of the salts of the bromo-acid.

Experiment showed this to be the case, and the preparation and investigation of the isomeric partially racemic hydrindamine chlorocamphorsulphonates are described in this section.

The analogy between the salts of the chloro-acid and the corresponding isomerides of the bromo-acid is on the whole very complete ; nevertheless, the  $\beta$ -salt of the former differs from that of the latter in one important particular, as it exists in two differently hydrated crystalline modifications which show an interesting behaviour.

The two salts are prepared by neutralising an aqueous solution of chlorocamphorsulphonic acid with hydrindamine, which is partly dissolved and partly suspended in water; the solution is then concentrated if necessary and allowed to cool. The first and several subsequent deposits seem to be homogeneous, and consist of bulky masses of very slender needles, but on further concentration the character of the crystalline deposit begins to change, and finally compact, transparent prisms are often obtained; by systematic crystallisation from water or very dilute alcohol, two different products may be isolated.

*$\alpha$ -Salt.*

The more sparingly soluble salt, which doubtless corresponds with the  $\alpha$ -salt of the bromo-acid, invariably separates from warm or cold water in bulky, opaque, or translucent masses consisting of very small, concentrically grouped needles, which under the microscope are quite transparent and appear to be fairly well defined.

These crystals liquefy almost immediately—in less than 5 minutes—in their water of crystallisation when they are heated at about  $100^{\circ}$  in a water-oven, giving a brittle, vitreous mass, from which the rest of the water is expelled only on prolonged heating; on exposure to the air, they gradually effloresce, and continue to lose in weight during many days, but even when efflorescence has ceased they still liquefy in their water of crystallisation when heated at  $100^{\circ}$ . In appearance and in all ordinary properties, this salt is difficult to distinguish from the  $\alpha$ -salt of the bromo-acid, but as a rule its crystals are rather larger and more definite. Compact, ill-defined prisms, such as are sometimes observed in the case of the  $\alpha$ -bromo-salt (p. 873), have never been obtained with this compound, although it has been repeatedly crystallised from water under different conditions; it also differs from the  $\alpha$ -salt of the bromo-acid, inasmuch as it is deposited in a crystalline, and not in an oily condition, from warm saturated aqueous solutions.

The  $\alpha$ -salt of hydrindamine and chlorocamphorsulphonic acid is only sparingly soluble in cold water, but it dissolves freely on warming, and is also readily soluble in cold chloroform and ethyl alcohol; it crystallises from methyl alcohol in long, transparent, efflorescent prisms, which often attain a length of several centimetres, but its solutions in chloroform give, on spontaneous evaporation, a vitreous or gum-like mass which apparently only becomes crystalline as the result of the absorption of atmospheric moisture. The anhydrous salt is only sparingly soluble in hot ethyl acetate, but in presence of a small quantity of water it dissolves freely, separating again as bulky, opaque masses.



The anhydrous salt has not a very definite melting point; it begins to sinter at about  $160^{\circ}$ , and then melts fairly sharply at about  $165$ — $166^{\circ}$  (corr.); it does not darken in colour appreciably when heated at  $100^{\circ}$  during several days.

The water of crystallisation was determined in two different samples. The first was prepared by crystallisation from methyl alcohol, and dried on porous earthenware during about 12 hours only.

0.5 lost 0.0413  $\text{H}_2\text{O}$  at  $100^{\circ}$  during 72 hours.  $\text{H}_2\text{O} = 8.26$ .

0.5 „ 0.0414  $\text{H}_2\text{O}$  „ „ „  $\text{H}_2\text{O} = 8.28$ .

The second sample was prepared in a similar manner, but was dried in the air until constant in weight.

1.0015 lost 0.0713  $\text{H}_2\text{O}$  at  $100^{\circ}$  during 72 hours.  $\text{H}_2\text{O} = 7.1$ .

1.000 „ 0.0701  $\text{H}_2\text{O}$  „ „ „  $\text{H}_2\text{O} = 7.0$ .

$\text{C}_{10}\text{H}_{14}\text{ClO} \cdot \text{SO}_3\text{H} \cdot \text{C}_9\text{H}_{11}\text{N} + 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 8.3$  per cent.

$\text{C}_{10}\text{H}_{14}\text{ClO} \cdot \text{SO}_3\text{H} \cdot \text{C}_9\text{H}_{11}\text{N} + 1\frac{3}{4}\text{H}_2\text{O}$  „  $\text{H}_2\text{O} = 7.3$  „

These results seem to show that the salt crystallises with  $2\text{H}_2\text{O}$ , of which it loses  $\frac{1}{4}$  mol. on exposure to the air; the experimental results agree with the calculated much more closely than in the case of the  $\alpha$ -salt of the bromo-acid, and it may also be noted that the two salts do not seem to be equally hydrated, although the difference is very small.

Determinations made by Carius' method with samples dried at  $100^{\circ}$  until constant gave the following results:

0.2844 gave 0.1037  $\text{AgCl}$ .  $\text{Cl} = 9.0$ .

0.1360 „ 0.0526  $\text{AgCl}$ .  $\text{Cl} = 9.4$ .

$\text{C}_{10}\text{H}_{14}\text{ClO} \cdot \text{SO}_3\text{H} \cdot \text{C}_9\text{H}_{11}\text{N}$  requires  $\text{Cl} = 8.8$  per cent.

### *$\beta$ -Salt.*

The hydrindamine chlorocamphorsulphonate, which is deposited from the mother liquors of the  $\alpha$ -salt, gives, after further fractional crystallisation, a product which in some respects is very similar to the  $\beta$ -salt of the corresponding bromo-acid. This product is very often deposited from aqueous solution in the form of small, lustrous, compact, transparent, well-defined prisms, which are indistinguishable in appearance from the crystals of the  $\beta$ -salt of the bromo-acid, and, like the latter, become opaque when warmed in contact with their mother liquor.

Very great difficulty and uncertainty, however, were first experienced with this  $\beta$ -salt, as for a long time it seemed impossible to obtain it free from the  $\alpha$ -isomeride.

Owing to the great difference in appearance between the opaque

masses of slender needles of the  $\alpha$ -salt and the small, transparent crystals of the  $\beta$ -isomeride, and owing to the fact that the melting points of the salts cannot be determined until the samples have been dried at  $100^{\circ}$  for many hours, the best method of testing the purity of a sample supposed to be the  $\beta$ -salt, at any rate, in the case of the hydrindamine bromocamphorsulphonate, is to recrystallise the sample from cold or tepid water; if any  $\alpha$ -salt is then deposited, its presence can be immediately detected by mere inspection, as it forms opaque, white patches on the transparent prisms.

Now on recrystallising, the compact prisms of the  $\beta$ -chloro-salt from water—in order to ensure the purity of the preparation—the salt was often deposited again in its original, apparently pure, condition, and as this recrystallisation, with or without fractionating, could often be repeated many times without the bulky crystals of the supposed  $\alpha$ -compound making their appearance, it seemed that the latter was absent; on continuing this testing, however, under apparently the same conditions as before, small, opaque masses of needles, looking exactly like crystals of the  $\alpha$ -salt would be deposited among the transparent prisms, sometimes simultaneously with the latter, generally only towards the end of the crystallisation; the opaque masses having been separated mechanically and the prisms again dissolved, the solution again deposited what were obviously two different kinds of crystals, and in some cases the opaque masses which appeared to be crystals of of the  $\alpha$ -salt were deposited alone.

As these recrystallisations were often carried out without altering, intentionally or appreciably, the quantity of water present, the solutions being of such a strength that the salt only separated after they had cooled to nearly atmospheric temperature, and as two kinds of crystals were certainly obtained, the presence of the  $\alpha$ -salt seemed to be the only explanation of the difficulty, and repeated attempts were made to get rid of this compound by fractional crystallisation, combined with a mechanical separation of the opaque masses, whenever they appeared.

#### *The $\beta$ -Salt Crystallises in Two Differently Hydrated Forms.*

Finding that these operations failed to alter the character of the deposits, the crystals, which were supposed to be those of the  $\alpha$ -salt, were collected and examined. They consisted of bulky masses of transparent needles, indistinguishable in appearance, even under the microscope, from the crystals of the  $\alpha$ -salt, and on recrystallisation from water or dilute methyl alcohol, they were deposited apparently unchanged, the only slight difference which could be observed between these and the crystals of the  $\alpha$ -salt was, that when heated in a water-

oven they did not liquefy in their water of crystallisation except after some time (20—30 minutes), whereas the  $\alpha$ -salt invariably does so in the course of a few minutes, even when it is thoroughly air-dried.

Although it seemed very improbable that this  $\beta$ -salt of the chloro-acid would differ from the  $\beta$ -salt of the bromo-acid to any considerable extent, the above observations doubtless indicated the existence of two different crystalline varieties of the latter, and as the result of further experiments, this view was fully confirmed.

The one crystalline form of the  $\beta$ -salt, which is called the A variety, as already stated, is very similar to, in fact indistinguishable from, the ordinary crystalline form of the  $\beta$ -salt of the bromo-acid (p. 874), and consists of small, lustrous, transparent, well-defined prisms, which are often massed together concentrically; these crystals do not seem to effloresce, and they become constant in weight after a few days' exposure to the air; they then contain about 3.7 per cent. of water, which is expelled on prolonged heating at 100°:

0.5	lost 0.019	H <sub>2</sub> O at 100° during 72 hours.	H <sub>2</sub> O = 3.9.
0.5190	„ 0.0195	H <sub>2</sub> O „ „ „	H <sub>2</sub> O = 3.7.
1.1885	„ 0.0444	H <sub>2</sub> O „ „ „	H <sub>2</sub> O = 3.7.
$C_{10}H_{14}ClO \cdot SO_3H, C_9H_{11}N + H_2O$ requires H <sub>2</sub> O = 4.3 per cent.			
$C_{10}H_{14}ClO \cdot SO_3H, C_9H_{11}N + \frac{3}{4}H_2O$ „ H <sub>2</sub> O = 3.2 „			

As the crystals of the  $\beta$ -salt of the bromo-acid give results which agree well with those required for  $\frac{3}{4}$  mol. H<sub>2</sub>O, it is rather surprising that this corresponding form of the  $\beta$ -salt of the chloro-acid should give values which are not in good agreement with the theoretical ones; for reasons which will appear later, it is possible that this is due to the presence of the other hydrated form of the  $\beta$ -salt.

The second crystalline form of the  $\beta$ -salt, the B variety, separates from water or dilute methyl alcohol in opaque masses of slender, transparent needles, indistinguishable by inspection from the crystals of the  $\alpha$ -salts of the chloro- and bromo-acids but absolutely different in appearance from the crystals of the A variety of this salt.

These crystals do not effloresce appreciably, and when air-dried they contain about 5.4 per cent. of water of crystallisation, which is only very slowly expelled at 100°, as the salt gradually liquefies at first, and then forms a vitreous mass.

0.5	lost 0.0265	H <sub>2</sub> O at 115° (4 hours), at 100° (12 hours).	H <sub>2</sub> O = 5.3.
0.4	„ 0.0222	H <sub>2</sub> O „ 100° during 16 hours.	H <sub>2</sub> O = 5.5.
$C_{10}H_{14}ClO \cdot SO_3H, C_9H_{11}N + 1\frac{1}{4}H_2O$ requires H <sub>2</sub> O = 5.3 per cent.			

These results agree satisfactorily with those required by the above formula, but too much weight should not be attached to them, as it is difficult to ascertain whether this B variety of the  $\beta$ -salt is, or is not,

free from the A form; the two kinds of crystals are often deposited together, and the presence of the A form might easily pass undetected.

Now since a determination of the water of crystallisation in the B variety of the  $\beta$ -salt, for the reason just given, may not be considered conclusive proof of its non-identity with the  $\alpha$ -salt, and as, so far, no other evidence has been advanced to show that the two substances are really different, it is necessary to state fully the facts which have led to the conclusion that the  $\beta$ -salt crystallises in two differently hydrated forms. The existence of any ordinary compound in two such forms is of course in no way remarkable, but in view of the possible conversion of one of these partially racemic salts into the other by crystallisation (compare the hydrindamine *cis*- $\pi$ -camphanates, p. 869), of the curious relation between the two crystalline hydrates of the  $\beta$ -salt, of the fact that the  $\beta$ -salt of the bromo-acid seems to exist in only one form, and of the great similarity between the  $\alpha$ -salt of the chloro-acid and the B variety of the  $\beta$ -salt, it cannot be denied that some further evidence is required in order to prove that the A and B crystalline varieties both represent  $\beta$ -salt.

Generally speaking, of course, it is a very simple matter to ascertain whether a substance which gives two kinds of crystals is a mixture or is dimorphous, but in this particular instance there were many difficulties in the way. It is useless, for example, to take the melting point of either the  $\alpha$ - or the  $\beta$ -salt, unless the crystals have been thoroughly dehydrated at 100°, an operation which requires about 24 hours. Further, the  $\beta$ -salt, even when thus treated, does not appear to have a definite melting point. Crystals of the A variety which have been heated at 100° during only a few hours or during several days, sometimes melt fairly sharply at about 130°, but other samples only sinter at about 140° and do not melt completely until about 165°. Most samples, in fact, behave much as they might be expected to do if they were really mixtures of the  $\alpha$ - and  $\beta$ -salts. This indefinite melting point may possibly be caused by the presence of water, as the dehydrated salt is very hygroscopic, or by the presence of two different crystalline varieties of the anhydrous salt, or by slight decomposition; but after the many determinations which have been made with various samples, it is impossible to believe that it is due to the presence of the  $\alpha$ -salt.

Another difficulty in settling this question of the existence of two forms of the  $\beta$ -salt was owing to the fact that the B variety varies very much in appearance and behaviour, according to the conditions under which it is deposited; although generally it forms opaque masses of minute needles, which, when dried on porous earthenware, do not melt in the water oven until after some time (30—60 minutes), in some cases when it has been deposited more slowly, it forms slightly

larger transparent prisms which, like the crystals of the  $\alpha$ -salt, liquefy completely in the course of a few minutes.

These statements merely show that a conclusion could not be hastily formed, and the evidence which is relied on to establish the existence of the two varieties of the  $\beta$ -salt has still to be given.

In the first place, then, the two forms A and B often change one into the other on recrystallisation from water or dilute methyl alcohol. Although the variety A may be recrystallised several times, 8, 10, or more, consecutively, without showing the presence of traces of the variety B in the deposit, and although, similarly, the variety B may often be recrystallised several times without passing into the form A, repeated crystallisation, without intentionally altering the quantity of solvent will cause, or, at any rate, has done hitherto, the conversion of one variety into the other, either partially or entirely. The  $\alpha$ -salt has been repeatedly crystallised under the same conditions as the  $\beta$ -salt, but it has never yet been observed to give crystals resembling those of the A variety of the  $\beta$ -salt.

In the second place, the specific rotations of the two varieties A and B, calculated for the anhydrous salts, are identical within the limits of experimental error, whilst the specific rotation of the  $\alpha$ -salt is lower than that of the  $\beta$ -salt (compare following section).

There can, therefore, be no doubt that the variety B of the  $\beta$ -salt is not the same substance as the  $\alpha$ -salt in spite of their outward similarity. The conditions which determine the formation of one or the other variety of the  $\beta$ -salt have not been satisfactorily determined, although presumably it is primarily a question of temperature. Experiments were made to ascertain the influence of a change in temperature, and it was found that when an aqueous solution of the  $\beta$ -salt was cooled to  $0^{\circ}$  before the separation of oil or of crystals commenced, the form B was deposited, and this occurred repeatedly. The same solution, when concentrated a little, and then allowed to crystallise at the ordinary temperature, gave crystals of the A variety three times consecutively. Moreover, solutions which are beginning to deposit the variety B, if warmed gently to about  $20^{\circ}$  without dissolving the whole of B, will often deposit the variety A on subsequent cooling.

On the other hand, the variety B often separates when the solutions crystallise at about  $15^{\circ}$ , at which temperature A is usually deposited. The presence of crystals of one or other variety in the solution does not seem to have any effect on the nature of the subsequent deposit. Solutions from which the form A has been deposited, and in which the crystals are still immersed, if left alone, will sometimes give specks of opaque B in the course of a few hours, but in other cases nothing of the kind happens, even after keeping during several days. The crystals of A in contact with the solution will also remain unaltered for

several days, but at the end of this time usually begin to change in appearance and become opaque at the edges. Whether this is due to the formation of a thin deposit of the B variety or to an actual change in the crystals themselves is difficult to determine. This conflicting evidence seems to show that the temperature at which the one variety changes into the other is within the limits of ordinary atmospheric temperatures, but it would also appear that the concentration of the solution has some effect. A solution which has given one of the two forms, if merely warmed until all the crystals have dissolved, will generally give the same variety again and again, and only on repeating these operations a number of times does the change into the other variety occur. The whole behaviour of the  $\beta$ -salt requires, in fact, a more complete investigation before it can be stated with certainty what are the conditions which determine the formation of one or other of these different hydrates.

It seemed probable, at one time, that the change which the  $\beta$ -salt sometimes undergoes on recrystallisation, might be caused by the resolution of the partially racemic compound into the two salts of the enantiomorphous bases, since Ladenburg has shown (*Ber.*, 1899, 32, 50) that partially racemic strychnine racemate has a definite transition temperature at which such a change occurs; the experiments described in the following section show, however, that this is not the case, and that the two varieties of the  $\beta$ -salt are both partially racemic.

As regards the ordinary properties of the  $\beta$ -salt little need be said; it is only sparingly soluble in cold water, but dissolves freely in cold ethyl or methyl alcohol.

#### *Molecular Weight Determinations.*

The molecular weight of the isomeric hydrindamine chlorocamphor-sulphonates was determined in dilute aqueous solution by the cryoscopic method; the results show that the two salts are largely dissociated, the values obtained being approximately half the calculated value.

	Weight of solvent.	Weight of substance.	Grams substance in 100 grams solvent.	Depression of freezing point.	M. W.
$\alpha$ -Salt .....	25 grams	0.3	1.2	0.100	227
	25 "	0.2	0.8	0.080	190
	25 "	0.3	1.2	0.100	227
$\beta$ -Salt .....	25 "	0.3	1.2	0.110	207

Taking the water of crystallisation to be 7.0 per cent. in the  $\alpha$ -salt and 3.7 per cent. in the  $\beta$ -salt (variety A), the values would become

$\alpha$ -Salt : M. W. = 200.

$\beta$ -Salt : M. W. = 199.



*Conversion of  $\beta$ - into  $\alpha$ -Salt.*

The close relationship between the isomeric hydrindamine bromo-camphorsulphonates and chlorocamphorsulphonates rendered it almost certain that the  $\beta$ -salt of the chloro-, like that of the bromo-acid, would be converted into the  $\alpha$ -isomeride on evaporation with the externally compensated base; experiment showed this to be so. If, after evaporating almost to dryness 5—8 times, small quantities of base being added after each evaporation, the residue is crystallised from water, it is deposited in needles identical in appearance with the crystals of the  $\alpha$ -salt, and when these needles have been dried for about 30 hours at  $100^\circ$ , they have no longer the indefinite melting point of the  $\beta$ -salt, but liquefy fairly sharply at  $162$ — $165^\circ$ .

*IV. Specific and Molecular Rotations of the Hydrindamine Chlorocamphorsulphonates.*

The determination of the specific rotations of the isomeric hydrindamine chlorocamphorsulphonates was undertaken with two objects; in the first place, in order to prove that the  $\beta$ -salt, in spite of its apparent behaviour to the contrary, is not really converted into the  $\alpha$ -isomeride on repeated crystallisation from water; and in the second place, in order to ascertain whether the analogy between the salts of the bromo- and chloro-acids would extend to their optical behaviour.

The first of these points, namely, the homogeneity and unalterability of the  $\beta$ -salt, had of course to be settled before the second could be considered, and the experiments which were made for this purpose may now be described.

A sample of the  $\beta$ -salt, which had been prepared by repeated recrystallisation from water, and which consisted entirely of the (A) variety so far as could be ascertained, was separated by further crystallisation into two approximately equal fractions, I and II, both of which were apparently identical with the original sample; the specific rotations of these two fractions were then determined in aqueous solution, the air-dried salt being used; both fractions contained 3.7 per cent. of water. A 200 mm. tube was used and the volume of the solution was 25 c.c. in both cases.

 *$\beta$ -Salt. (A) Variety.*

			Calc. for anhydrous salt.	
	$\alpha_D$ .	$[\alpha]_D$ .	$[\alpha]_D$ .	$[M]_D$ .
I. 0.25	+ 58'	+ 48.3°	+ 50.2°	+ 201°
0.5	1°57'	48.8	50.7	202
II. 0.25	57'	47.5	49.3	197
0.25	59'	49.1	50.9	203

A sample of the  $\beta$ -salt, which had been deposited in the opaque, bulky crystals of the B variety, and which was indistinguishable from the  $\alpha$ -salt in appearance, was then examined. The observations were made in aqueous solution in a 200 mm. tube, the volume of the solution being 25 c.c.; the air-dried salt, which was afterwards found to contain 5.2 per cent. of water of crystallisation, was employed.

	$[\alpha]$	$[\alpha]_D$	Calc. for anhydrous salt.	
			$[\alpha]_D$	$[M]_D$
0.5 gram .....	+1°56'	+48.4°	+51°	+200
0.5 " .....	1°55'	47.9	50.5	202

Another sample of the variety B, obtained in a different crystallisation, was also examined under the same conditions, with the following result:

$$0.5 \text{ gram} \dots \dots \alpha + 1^\circ 58'. \quad [\alpha]_D + 49.1^\circ.$$

The water of crystallisation in this (air-dried) sample was not determined, but taking it to be 5.2 per cent., as in the previous case, the values for the anhydrous salt would be

$$[\alpha]_D + 51.8^\circ. \quad [M]_D + 207.$$

These results, under ordinary circumstances, would be sufficient to establish the chemical identity of the two different crystalline varieties of the  $\beta$ -salt, especially as the samples recovered from the solutions used in the above experiments could be converted one into the other just as can ordinary preparations of the  $\beta$ -salt.

It must be stated, however, that in one case the examination of the crystalline variety B led to very different results; two portions of one and the same sample, which contained 5.2 per cent. of water, were separately dissolved in cold water, the solutions diluted to 25 c.c., and examined in a 200 mm. tube.

	$\alpha_D$	$[\alpha]_D$	Calc. for anhydrous salt.	
			$[\alpha]_D$	$[M]_D$
0.25 gram .....	+1°6'	+54.5°	+57.4°	+229
0.25 " .....	1°4'	53.5	56.4	225

It will be seen that these values differ very widely from all those previously obtained, and as the difference could not be caused by the presence of the  $\alpha$ -salt—which has a lower specific rotation than the  $\beta$ -salt—it seemed possible that a partial resolution of the  $\beta$ -salt had been accomplished. In order to confirm or disprove this view, the sample used in the last two experiments was fractionally crystallised in water, and again obtained, after one or two unsuccessful attempts, the crystalline variety B. The latter was separated, dried in the air, and examined again under the same conditions



as before (volume = 25 c.c. ; column = 200 mm.). The sample was found to contain 6·8 per cent. of water.

		Calc. for anhydrous salt.		
		$[\alpha]_D$	$[\alpha]_D$	$[M]_D$
I. 0·5 gram.....	+1°58'	+49·15°	+52·6°	+210
II. 0·4 „ .....	1°34'	48·9	52·4	209

These results agree moderately well with those obtained for the specific rotation of the original samples of the variety A, but the very abnormal values obtained for the variety B in the preceding experiment, combined with the extraordinary behaviour of the isomeric hydrindamine *cis*- $\pi$ -camphanates (compare pp. 910, *et seq.*), raised suspicion as to the homogeneity of the  $\beta$ -salt and the constancy of its specific rotation in the two different crystalline forms.

A fresh sample of the  $\beta$ -salt was, therefore, crystallised from water and separated into three fractions. The first deposit consisted of the variety A ; it was dried in the air until constant, and it was then taken as containing 3·7 per cent. of water. The second crop consisted of the variety B, and when air-dried contained 5·5 per cent. of water. The third crop also consisted of the variety B, and when air-dried contained 6·0 per cent. of water.

The specific rotations of the air-dried fractions were determined in aqueous solution ; volume = 25 c.c. ; column of liquid, 200 mm.

			Calc. for anhydrous salt.		
		$\alpha$ .	$[\alpha]_D$ .	$[\alpha]_D$ .	$[M]_D$ .
I. (A).	0.5 gram	+1°52'	+46.7°	+48.5°	+194
II. (B).	0.5 „	1 56	49.0	51.8	207
III. (B).	0.5 „	1 52	46.6	49.5	198

The first fraction (A variety), crystallised again from water, gave a deposit of the variety A ; this was dried in the air, and examined under the same conditions as above.

0·5 gram (variety A).  $\alpha$  +1°55'.  $[\alpha]_D$  +47·95°.

This sample was found to contain 3·45 per cent. of water, so that the specific and molecular rotations of the anhydrous salt are :

$[\alpha]_D$  +49·6°.  $[M]_D$  +198°.

It may be concluded from these results, firstly, that the two crystalline varieties of the  $\beta$ -salt become identical in solution, and that neither is identical with the  $\alpha$ -salt ; secondly, that the formation of the crystalline variety (B) of the  $\beta$ -salt is not caused by a resolution of that salt into different optically active components which are separable by fractional crystallisation.

It will, perhaps, be noted that the results obtained in all these experiments with the  $\beta$ -salt, excluding the two very abnormal values on p. 898, which are possibly due to some large experimental error, vary from  $[\alpha]_D + 48.5^\circ$  to  $+52.6^\circ$  in solutions of practically the same concentration; this want of agreement is probably caused in some measure by unavoidable errors introduced in allowing for the water of crystallisation. During the prolonged heating at  $100^\circ$ , which is required before the salt becomes fairly constant in weight, it evidently undergoes slight decomposition, and on subsequent treatment with water, it gives a slightly coloured and faintly turbid solution; hence the loss, which is attributed to water of crystallisation, may be partly due to other changes.

*Specific and Molecular Rotations of the Isomeric Salts.*

For the second main object of the optical examination of these compounds, namely, the comparison of the specific and molecular rotations of the  $\alpha$ - and  $\beta$ -salts with one another, and with those of the corresponding salts of the bromo-acid, experiments were made in three different solvents, as in the case of the last-named compounds.

The specific rotation of the  $\alpha$ -salt was first determined in aqueous solution with an air-dried sample containing 7.05 per cent. of water of crystallisation; the volume of the solution was 25 c.c., and a 200 mm. tube was employed in all cases.

Calc. for anhydrous salt.					
		$\alpha_D$	$[\alpha]_D$	$[\alpha]_D$	$[M]_D$
(1)	0.25 gram	$+52'$	$+43.3^\circ$	$+46.5^\circ$	+186
(2)	0.25 "	$48'5$	40.3	43.3	173
(3)	0.25 "	$54'$	45.0	48.3	193
(a)	0.5 "	$1^\circ43'$	43.0	46.2	185
(b)	0.5 "	$1^\circ46'$	44.1	47.5	190

Excepting (2), the results are sufficiently concordant, and give for the molecular rotation  $[M]_D$  a mean value +188.

Now the mean value for the molecular rotation of the  $\beta$ -salt, calculated from the most concordant results given above, is +202, so that in dilute aqueous solution the two isomerides have but slightly different molecular rotations; this difference practically disappears in dilute alcoholic solutions, but becomes more marked in chloroform solutions.

*Alcoholic Solutions.  $\alpha$ -Salt.*—An air-dried sample containing 7.05 per cent. of water was used in these experiments; the solvent was 75 per cent. ethyl alcohol, volume of the solution 25 c.c., and length of the tube 200 mm.

		Calc. for anhydrous salt.		
	$\alpha_D$	$[\alpha]_D$	$[\alpha]_D$	$[M]_D$
1 gram	+4°12'	+52·6°	+56·6°	+226
1 „	4°8'	51·7	55·6	222

*$\beta$ -Salt.*—This salt was examined under exactly the same conditions, but three different samples were used, and one of them (1) had been dried at 100°; the other two (2 and 3) were air-dried samples of the crystalline variety A, and were taken as containing 3·7 per cent. of water.

		Calc. for anhydrous salt.		
	$\alpha_D$	$[\alpha]_D$	$[\alpha]_D$	$[M]_D$
(1) 0·5190 gram	+2°13'·5	+53·6°	+53·6°	+214
(2) 0·5 „	2°8'	53·4	55·4	221
(3) 1·0 „	4°11'	52·5	54·5	218

It is possible that prolonged heating at 100° may effect the specific rotation of the  $\beta$ -chloro-salt, just as it seems to do in the case of the  $\beta$ -bromo-salt, and, neglecting the result of experiment (1), the specific and molecular rotations of the isomeric chloro-salts become practically identical.

*Chloroform Solution.*—Air-dried samples were used in both cases; the volume of the chloroform solution was 25 c.c., and a 200 mm. tube was used.

$\alpha$ -Salt: 0·5 gram	$\alpha_D + 1°16'$	$[\alpha]_D + 31·3°$
$\beta$ -Salt: 0·5 „	$\alpha_D + 1°42'$	$[\alpha]_D + 42·5°$

As the variety (A) of the  $\beta$ -salt was used, it may be taken as containing 3·7 per cent. of water; the  $\alpha$ -salt contained 7·05 per cent. The values for the anhydrous substances would therefore be the following:

$\alpha$ -Salt:	$[\alpha]_D + 33·6°$	$[M]_D + 134$
$\beta$ -Salt:	$[\alpha]_D + 44·1°$	$[M]_D + 176$

#### *Molecular Rotation of Chlorocamphorsulphonic Acid.*

Before comparing the molecular rotations of the isomeric salts of chlorocamphorsulphonic acid with those of the corresponding derivatives of the bromo-acid, it was necessary to determine the molecular rotation of the first-named acid.

The only data available for this purpose were those obtained some time ago by Kipping and Pope, who determined the specific rotations of the sodium and barium salts of chlorocamphorsulphonic acid in aqueous solution (Trans., 1893, 63, 601). The values then obtained were  $[\alpha]_D + 63·8°$  in the case of the sodium salt and  $[\alpha]_D + 46·8°$  in that

of the barium salt, from which the molecular rotation  $[M]_D$  is calculated to be +184 and +177 respectively.

For the purpose of obtaining further information on this point, ammonium chlorocamphorsulphonate was prepared; this salt, judging by analogy, should give in 1—2 per cent. aqueous solution values for the molecular rotation of the acid which could be satisfactorily compared with those obtained in the case of the isomeric hydrindamine salts and also with those of the hydrindamine bromocamphorsulphonates.

Samples of this ammonium salt, dried at  $100^\circ$ , were examined optically in aqueous solution in a 200 mm. tube.

Weight of salt.	Volume of solution.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
0.25 gram.	25 c.c.	+1°19.5'	+66.25°	+187
0.25 "	"	1°18.5'	65.5	185
0.5 "	"	2°41'	67.0	190

The mean of these concordant results gives a molecular rotation  $[M]_D$  +187, a value which agrees well with those obtained in the case of the sodium and barium salts, but which is a little higher than both of these, just as the molecular rotation of the bromo-acid, deduced from an examination of its ammonium salt, is a trifle higher than the value obtained by Walden (compare p. 886).

On now comparing the molecular rotations of the isomeric hydrindamine salts of chlorocamphorsulphonic acid with the value just obtained, it will be seen that the  $\alpha$ -salt shows the normal behaviour, whilst the molecular rotation of the  $\beta$ -salt is a little too high.

$\alpha$ -Salt:  $[M]_D$  +188. Acid:  $[M]_D$  +187.  $\beta$ -Salt:  $[M]_D$  +202.

The difference in the case of the latter, however, is almost insignificant, and the only reason why attention is drawn to it is because in the case of the hydrindamine bromocamphorsulphonates, the conditions are reversed, the  $\beta$ -salt having a molecular rotation below the normal value (compare p. 885).

Considering the results of the optical examination as a whole, the behaviour of the hydrindamine chlorocamphorsulphonates is obviously analogous to that of the isomeric salts of the bromo-acid, and the results also show that the two chloro-salts are both partially racemic substances; any possibility of a resolution of the externally compensated base having occurred in the case of the salts of the bromo-acid is thus excluded, as there can be no doubt that the isomerism of the chloro-salts is due to the same cause as that of the  $\alpha$ - and  $\beta$ -bromo-salts.

### V.—*Hydrindamine cis- $\pi$ -Camphanates.*

In order, if possible, to obtain further examples of isomeric partially racemic salts, the investigation of which might help to explain the existence of the isomeric hydrindamine bromo- and chloro-camphorsulphonates, it seemed desirable in the first place to try and prepare such isomerides from the same base as before, namely, externally compensated hydrindamine, but using an acid altogether different from those already employed.

Now optically active monobasic acids which give stable, well-crystallised salts, with the exception of the sulphonic acids of camphor and its derivatives, are not easily obtainable, but among the new derivatives of camphor recently investigated there occurred an acid which seemed suitable for the purpose in view, namely, *cis- $\pi$ -camphanic acid* (Trans., 1896, 69, 943).

*cis- $\pi$ -Camphanic acid*, as previously shown, is a lactonic monocarboxylic acid of the composition  $C_{10}H_{14}O_4$ ; as it is practically insoluble in cold water and only sparingly soluble in most ordinary organic solvents, it seemed probable that it might give, with externally compensated hydrindamine, salts which would crystallise readily, and which might possibly exist in isomeric forms. Experiment showed this supposition to be well founded, and the properties of two isomeric hydrindamine *cis- $\pi$ -camphanates* are described in this section of the paper.

Before passing to the consideration of these salts, it may be stated that the acid is a well-defined substance which shows very great stability in many ways, and the lactonic ring contained in it is not readily hydrolysed by sodium hydroxide solution at ordinary temperatures; it is, at the same time, a comparatively feeble acid, and some of its salts, as, for example, its quinoline and ammonium salts (*loc. cit.*), undergo hydrolytic dissociation very readily in aqueous solution.

The study of the isomeric hydrindamine *cis- $\pi$ -camphanates* has shown that these two compounds are both partially racemic salts, and their formation may therefore be explained in the same way as that of the isomeric hydrindamine bromocamphorsulphonates (p. 868) and chlorocamphorsulphonates, namely, by assuming that the negative acid ion becomes united to nitrogen valencies, which being those of a nitrogen atom contained in an enantiomorphous compound, are necessarily differently situated.

In accordance with this view, the more readily soluble salt can be partially converted into the isomeride by repeated evaporation with an aqueous solution of the externally compensated base.

The isomeric hydrindamine *cis- $\pi$ -camphanates* differ, however, from

the salts of the sulphonic acids in undergoing hydrolytic dissociation to some extent in aqueous and in aqueous alcoholic solutions, and this difference in behaviour has the important consequence that the salts are partially converted one into the other on solution in these solvents; this, for the reasons already given (p. 869), was to be expected.

Owing to the fact that *cis*- $\pi$ -camphanic acid is practically insoluble in cold water, it was easy to prove that its isomeric salts do not represent salts of enantiomorphous hydrindamines (p. 909); the question of the possible autoracemisation of the optically active base being considered as an explanation of the formation of the various isomeric salts described in these papers is therefore definitely answered in the negative.

#### *Preparation of the Salts.*

*cis*- $\pi$ -Camphanic acid is dissolved in methyl alcohol and an aqueous or alcoholic solution of hydrindamine is added until a permanent alkaline reaction is obtained; on evaporating the solution to a small volume and then adding methyl alcohol, and allowing to cool, the salt is deposited in colourless needles, and by repeated fractional crystallisation at different temperatures, preferably from ethyl alcohol, the product is separated into two components.

#### *$\alpha$ -Salt.*

The more sparingly soluble salt, hereafter referred to as the  $\alpha$ -compound, melts almost sharply at about 193°, when it is heated fairly quickly from about 100°, but as it slowly decomposes and turns brown even at comparatively low temperatures, its melting point depends to some extent on the rate of heating. It crystallises from ethyl alcohol and other solvents in slender, concentrically grouped prisms or needles, which are deeply striated, and appear to consist of bundles of smaller crystals, and it dissolves fairly easily in boiling alcohol and water, but is only sparingly soluble in cold ethyl acetate, ether, or boiling chloroform. When crystallised from methyl alcohol containing acetone, it soon darkens in colour, and after some time a considerable quantity of tarry matter is formed.

#### *$\beta$ -Salt.*

The more readily soluble salt, which will be referred to as the  $\beta$ -salt, melts and decomposes slightly at about 173°, but here again the melting point depends to some extent on the rate of heating; in appearance, and in all other ordinary properties, the  $\beta$ -salt resembles the  $\alpha$ -compound very closely, but its crystals are usually smaller and its solubility is greater than that of the latter.

The relative quantities of the two salts obtained after repeated fractional crystallisation were determined in one experiment and found to be 1·8 grams of the pure  $\alpha$ -salt and 3·1 grams of the  $\beta$ -compound, together with about 2·0 grams of a mixture of the two melting at about 168°. In spite of the difference in melting point of the two salts, it is, however, a very difficult matter—if not impossible—to make sure that the  $\beta$ -compound is free from the  $\alpha$ -salt, as its melting point is not very much altered by the presence of a small quantity of the latter, and a mixture of approximately equal quantities of the two salts only sinters at about 165°, melting almost completely at about 170°. For this reason, the fraction melting at about 168°, referred to above, must not be considered to represent  $\beta$ -salt; it is more probably a mixture of approximately equal quantities of the two components.

It will be seen from these numbers that the quantities of the  $\alpha$ - and  $\beta$ -salts are probably much more nearly equal than in the case of the  $\alpha$ - and  $\beta$ -salts of hydrindamine bromocamphorsulphonic acid, and that whereas in the latter case the relative quantity of the  $\beta$ -salt is very small, the  $\beta$ -*cis*- $\pi$ -camphanate is probably formed in rather larger quantities than the  $\alpha$ -salt.

#### *The Salts are Isomeric.*

Since *cis*- $\pi$ -camphanic acid is a lactonic monocarboxylic acid, which when boiled with a solution of sodium hydroxide is converted into a salt of a hydroxydicarboxylic acid (Kipping, *Trans.*, 1896, 69, 945), little interest could be attached to these two salts until it had been proved that they are isomeric, for the one might have been derived from the lactonic monocarboxylic acid, the other from the hydroxydicarboxylic acid.

Now the percentage composition of the normal salt of a *cis*- $\pi$ -camphanic acid differs but little from that of the normal salt of the hydroxydicarboxylic acid, as will be seen from the following numbers :

$C_{10}H_{14}O_4, C_9H_{11}N$  requires C=68·8; H=7·5; N=4·2 per cent.

$C_{10}H_{16}O_5, 2C_9H_{11}N$  „ C=69·8; H=7·6; N=6·9 „

The results of combustions would not, therefore, decide satisfactorily between the two possible formulæ, and nitrogen determinations would probably have given results intermediate between the two values 4·2 and 6·9.

Under these circumstances, the following methods were adopted to establish the isomerism of the two compounds :

Firstly, both salts were separately dissolved in methyl alcohol, the solutions rendered distinctly alkaline with hydrindamine, and then

heated on the water-bath in closed vessels during about 3 hours; at the end of this time, both solutions, which were still alkaline, were allowed to evaporate spontaneously. The deposits melted at  $173^{\circ}$  and  $193^{\circ}$  respectively, showing that the two salts had not been appreciably changed by this treatment; had one of them been derived from a mono-, the other from a di-carboxylic acid, the former should have been converted into the latter under the conditions of the experiment, and the solution should have become neutral.

Both salts are anhydrous. After recrystallisation from methyl alcohol and ether, finely divided samples were dried in the air during 2 days and then heated at  $100^{\circ}$  during 1 hour; the  $\alpha$ -salt lost only 0.8 per cent., the  $\beta$ -salt 1.8 per cent., the percentage of water required for  $C_{10}H_{14}O_4, C_9H_{11}N + \frac{1}{2}H_2O$  being 2.6 per cent. On further heating at  $100^{\circ}$ , both salts continued to lose in weight very slowly, and after 24 hours heating, the total loss amounted to 4.2 per cent. in the case of the  $\alpha$ - and 8.4 per cent. in the case of the  $\beta$ -compound; as, however, both compounds had turned brown, the  $\beta$ -salt especially, and their weights had not become constant, it must be concluded that the loss on heating is due to decomposition and volatilisation of the base.

For the further analysis of the two compounds, the samples were dried over sulphuric acid.

The determination of the percentage of hydrindamine in the two salts offered the best means of deciding between the two possible formulae, and this was done in two ways.

In the first method, a weighed quantity of the salt was treated with excess of a solution of barium hydroxide in a current of steam, the base collected in hydrochloric acid, the solution evaporated to dryness, and the residue of hydrindamine hydrochloride weighed; the results were as follows:

$\alpha$ -Salt. 0.4 gave 0.1924  $C_9H_{11}N, HCl$ .  $C_9H_{11}N = 37.7$ .

$\beta$ -Salt. 0.4 „ 0.1984  $C_9H_{11}N, HCl$ .  $C_9H_{11}N = 39.1$ .

$C_{10}H_{14}O_4, C_9H_{11}N$  requires  $C_9H_{11}N = 40.2$  per cent.

$C_{10}H_{16}O_5, 2C_9H_{11}N$  „  $C_9H_{11}N = 51.3$  „

Control experiments were made with hydrindamine hydrochloride under exactly the same conditions, and the following results were obtained:

0.2008 gave 0.1954  $C_9H_{11}N, HCl$  or 97 per cent. of the theoretical.

0.1969 „ 0.1835  $C_9H_{11}N, HCl$  „ 93 „ „ „

In the second analytical method, a weighed quantity of the salt was dissolved in the smallest possible quantity of hot methyl alcohol, the solution treated with a slight excess of concentrated hydrobromic



acid, and then evaporated, first on a water-bath until nearly dry, and then over potash and sulphuric acid; after about 2 days, the residues were nearly constant in weight, but a further loss of about 2 milligrams occurred in the course of about a fortnight.

$\alpha$ -Salt. 0.3 gave 0.3741  $C_9H_{11}N, HBr + C_{10}H_{14}O_4$ .

$\beta$ -Salt. 0.3 ,, 0.3745  $C_9H_{11}N, HBr + C_{10}H_{14}O_4$ .

Calculated for  $C_{10}H_{14}O_4, C_9H_{11}N$  residue = 0.3734.

,, ,,  $C_{10}H_{16}O_5, 2C_9H_{11}N$  ,, = 0.4305.

These results, especially those obtained by the last method, which is the more satisfactory of the two, prove that the two salts are isomeric, and that they are both normal salts of the lactonic monocarboxylic acid; it may also be stated that the acid which is liberated from the two salts on addition of hydrobromic acid is unchanged *cis*- $\pi$ -camphanic acid, easily recognisable by its highly characteristic crystalline form.

*Both the  $\alpha$ - and  $\beta$ -Salts give Optically Inactive Base.*

The next point to decide was whether the externally compensated base had been resolved into its enantiomorphous components by fractional crystallisation of the salts which it forms with *cis*- $\pi$ -camphanic acid. For this purpose, a small quantity (0.4 gram) of the  $\alpha$ -salt was decomposed with aqueous barium hydroxide, the base separated by steam distillation and collected in hydrochloric acid; the solution of the hydrochloride was concentrated to about 15 c.c. and then examined in a 200 mm. tube, but no rotation could be observed; a repetition of the experiment, using a larger quantity of the salt, gave the same result.

It is obvious, then, that the externally compensated base has not been resolved into its optically active components, and consequently it seems very probable that the isomerism of these two salts is due to the same cause as that which holds in the case of the  $\alpha$ - and  $\beta$ -salts of the bromo- and chloro-camphorsulphonic acids.

For this reason, it seemed quite unnecessary to repeat all the experiments which were made in the case of the bromo-salts in order to prove that the isomerides contain one and the same base.

*Conversion of the  $\beta$ - into the  $\alpha$ -Salt.*

The conversion of the  $\beta$ - into the more sparingly soluble  $\alpha$ -isomeride can be accomplished by evaporating its aqueous or alcoholic solution with a small quantity of hydrindamine; the change, however, does not take place very readily, possibly because the quantity of the  $\beta$ -salt in equilibrium with the  $\alpha$ -isomeride is larger than in the case of the bromocamphorsulphonic salts; after one or two evaporations, the

product melts over a wide range of temperature, and is doubtless a mixture of the two isomerides, but on repeated treatment, its melting point rises, becomes more definite, and finally reaches that of the  $\alpha$ -salt.

#### *Hydrolytic Dissociation of the Two Salts.*

The  $\alpha$ - and  $\beta$ -salts of *cis*- $\pi$ -camphanic acid differ from the hydrindamine bromo- and chloro-camphorsulphonates in undergoing hydrolytic dissociation in aqueous and alcoholic solutions; on boiling a solution of either salt in dilute methyl alcohol, hydrindamine is slowly evolved, a litmus paper suspended in the vapour very slowly turns blue, and the solution acquires an acid reaction.

Hydrolytic dissociation takes place to such a limited extent, however, that, judging by their melting points, the salts are not appreciably altered by crystallisation from methyl or ethyl alcohol; even when their solutions in a large volume of these solvents have been heated for some time and then evaporated almost to dryness, the crystalline deposits, after having been merely spread on porous earthenware, have the melting points of the original preparations. This statement does not imply that the salts are unchanged; it is, as already mentioned, a matter of considerable difficulty to prove that the  $\beta$ -salt is really free from its isomeride.

In discussing the nature of these isomeric salts, it was pointed out that, according to the explanation suggested, hydrolytic dissociation should bring about the partial conversion of one isomeride into the other; experiments were therefore made in order to ascertain whether this could be done in the case of these *cis*- $\pi$ -camphanates, which are doubtless hydrolytically dissociated to some extent.

For this purpose, an aqueous solution of the  $\beta$ -salt was heated during several hours on the water-bath, then evaporated to dryness, and the residue recrystallised from a small quantity of alcohol; the deposit sintered at about  $165^{\circ}$ , and did not melt completely until about  $175^{\circ}$ ; on repeating the above treatment, the deposit melted through approximately the same range of temperature; there is thus presumptive evidence that a partial conversion of the  $\beta$ - into the  $\alpha$ -salt had occurred. Since, under the above conditions, some hydrindamine is lost during evaporation, the indefinite melting point of the product might possibly have been due to the presence of *cis*- $\pi$ -camphanic acid, and, as a matter of fact, on repeatedly evaporating such a solution of the  $\beta$ -salt, and then crystallising from alcohol, the first deposit consists almost entirely of crystals of this acid.

In order to try and eliminate this source of inaccuracy, the experiment was carried out differently. A small quantity of the  $\beta$ -salt was dissolved in hot water, the solution placed in a closed vessel and

left at the ordinary temperature during several days; the solution was then allowed to evaporate to dryness spontaneously. The deposit thus obtained was evidently a mixture of the  $\alpha$ - and  $\beta$ -salts, as it melted from about 165—180°.

The  $\alpha$ -salt, treated with water in an exactly similar manner, seems to be partially converted into the  $\beta$ -salt, as the deposit thus obtained melts from about 185—190°; the change, however, seems to be only a very partial one, probably because the  $\beta$ -salt which is produced is gradually reconverted into the  $\alpha$ -isomeride during the slow crystallisation.

*The Enantiomorphous Hydrindamines have not been separated.*

The determinations of the specific rotations of the isomeric hydrindamine bromocamphorsulphonates and chlorocamphorsulphonates, and the fact that the  $\alpha$ - and  $\beta$ -isomerides do not change one into the other on solution in a large volume of water, prove that, if these isomerides are really the salts of enantiomorphous hydrindamines, the optically active base does not undergo autoracemisation when its salts are electrolytically dissociated. Now the salts of *cis*- $\pi$ -camphanic acid probably do undergo a partial change one into the other in aqueous solution, as just stated, but this is doubtless the result of hydrolytic dissociation only. Since, then, it may be taken as proved that the base ions do not racemise, if the base of the  $\alpha$ - or  $\beta$ -salt of any one of the three acids can be transferred to an optically inactive acid without being at any time set free from combination, an examination of the new salt would show whether the base was or was not optically active, and thus the question of the possibility of the salts being those of enantiomorphously related bases would be definitely settled.

In the case of the salts of the sulphonic acids, it was not very easy to carry out such an experiment satisfactorily, as the acids are both very readily soluble in water, and could not well be separated from the new salt; but *cis*- $\pi$ -camphanic acid being practically insoluble, its isomeric salts were very suitable for the purpose in view, and were therefore examined as follows.

A quantity (2 grams) of the  $\beta$ -salt, in a finely divided condition, was triturated with excess of concentrated hydrochloric acid, and after keeping for a few minutes the liberated *cis*- $\pi$ -camphanic acid was separated by filtration from the solution of hydrindamine hydrochloride; the residue was washed with a little ice-cold water, and the combined filtrate and washings, having been made up to about 15 c.c., were examined in a 200 mm. tube. The average of eight concordant readings gave  $\alpha = 0.6'$ .

This feeble levorotation was certainly due to the presence of a small

quantity of *cis*- $\pi$ -camphanic acid, which is not absolutely insoluble in cold water, and which has a specific rotation of about  $-24^\circ$  in dilute aqueous solution.

The contents of the tube and washings were then evaporated to dryness, the residual hydrindamine hydrochloride dissolved in cold water, and the solution filtered from a very small deposit of *cis*- $\pi$ -camphanic acid. On then diluting to about 15 c.c., and again examining the solution in a 200 mm. tube, it gave  $\alpha - 0.2^\circ$  and the same rotation, within the limits of experimental error, was shown by a cold saturated aqueous solution of *cis*- $\pi$ -camphanic acid.

It is thus proved that the base of the  $\beta$ -salt is optically inactive, and a similar experiment with a small quantity of the  $\alpha$ -salt gave the same result; as the base was at no time in the free state during the conversion of these salts into the hydrochloride, and as the base does not undergo autoracemisation in a state of combination, it is thus proved that the  $\alpha$ - and  $\beta$ -salts of *cis*- $\pi$ -camphanic acid both contain equal quantities of *d*- and *l*-hydrindamines.

#### VI.—*Specific and Molecular Rotations of the Hydrindamine cis- $\pi$ -Camphanates.*

Of the results obtained in the study of the isomeric salts which have now been described, not the least interesting and, at the same time, the most difficult to explain satisfactorily, are those which have accrued during the optical examination of the isomeric hydrindamine *cis*- $\pi$ -camphanates.

From the numerous observations which have been made, and which are recorded in this section, it would seem that different preparations of the  $\alpha$ -salt, all of which have the same, and a fairly sharp, melting point, have totally different specific rotations in methyl alcoholic solution, the values ranging from  $[\alpha]_D - 8^\circ$  to  $+20^\circ$ ; different samples of the  $\beta$ -salt also gave values ranging from  $[\alpha]_D - 10^\circ$  to  $-20^\circ$ , although the samples melted at the same temperature.

Now, in the case of the  $\beta$ -salt, this comparatively small variation in specific rotation might possibly be due to the presence of small quantities of the  $\alpha$ -isomeride, but in the case of the latter, where the difference in the specific rotation of different preparations is most marked, no such explanation is possible, as the quantity of  $\beta$ -salt which would be required to produce the observed result would be so large that its presence could not fail to be detected by ordinary examination.

Another remarkable fact brought to light is that the  $\alpha$ -salt shows ~~no~~ rotation in methyl alcoholic solution in a very marked manner,

whilst in the case of the  $\beta$ -isomeride a corresponding change has not been detected with certainty.

This difference in behaviour between two salts, otherwise so similar, recalls another instance already recorded, namely, the existence of two differently hydrated forms of the  $\beta$ -salt of hydrindamine chloro-camphorsulphonate and of only one form of the corresponding compound of the bromo-acid.

The discussion of these results is best postponed until the experimental data have been given, but it may be stated here that in dilute aqueous solution, the molecular rotations of the isomeric hydrindamine *cis*- $\pi$ -camphanates appear to be normal on the assumption that the salts are both partially racemic substances.

#### *Specific Rotation of the $\alpha$ -Salt.*

The determination of the specific rotation of the  $\alpha$ -salt was found to be a matter of considerable difficulty, and a large number of experiments had to be made.

The sample which was first examined had been heated at 100° for some time, and as slight decomposition had occurred, the result may not be very trustworthy; the solvent was 99.8 per cent. methyl alcohol, the volume of the solution 25 c.c., and the column of liquid 200 mm.

Exp. I. 0.2991 gram.  $\alpha + 43.3$   $[\alpha]_D + 30^\circ$ .

For the next determination, a different sample, obtained by crystallisation from ethereal alcohol, was used; this preparation was dried over sulphuric acid, the solvent and other conditions remaining the same.

Exp. II. 0.3 gram.  $\alpha + 18'$ .  $[\alpha]_D + 12.5^\circ$ .

This result differed so widely from the preceding one that a third specimen of the  $\alpha$ -salt was prepared; the sample, which melted sharply at 193° was dried at 100° during a few minutes only, and examined under the same conditions as before.

Exp. III. 0.3 gram.  $\alpha - 3'$ .  $[\alpha]_D - 2^\circ$ .

Here again, an entirely different value was obtained, although the three preparations used in these three experiments had all exactly the same melting point, and seemed in other respects to consist of pure  $\alpha$ -salt.

Now, it has already been pointed out that the  $\alpha$ -salt is partially transformed into the  $\beta$ -isomeride on solution in water, owing to the occurrence of hydrolytic dissociation (p. 908), but so far as can be ascertained, the change is comparatively limited, even when the solution has been kept during several days; consequently, it seemed very improb-

able that mere solution in methyl alcohol would bring about a similar transformation to such an extent as to appreciably alter the specific rotation, especially as it had been proved that alcoholic solutions of the  $\alpha$ -salt might be heated and evaporated without the melting point of the salt being obviously changed.

However, in order to ascertain whether prolonged treatment with such alcoholic solvents produced any change in the specific rotation, the whole of the solution used in Exp. III, together with the washings of the tube, &c., was evaporated nearly to dryness, again diluted to 25 c.c. with 99.8 per cent. methyl alcohol, and examined as before in a 200 mm. tube.

Exp. IV. 0.3 gram.  $\alpha \pm 0$ .

This result bears out the view that the  $\alpha$ -salt undergoes no appreciable change into the (laevorotatory)  $\beta$ -salt when it is dissolved in and heated with methyl alcohol.

The experimental error in dealing with such feebly active solutions is of course so large that little weight can be attached to the actual numerical results of Exps. III and IV, but it is obvious that if any change in specific rotation occurs it is a very small one.

As it appeared from the first three determinations that samples of the  $\alpha$ -salt of identical melting point may have a specific rotation ranging over very wide limits, a second series of experiments was made.

A fresh sample of the  $\alpha$ -salt was prepared, dried over sulphuric acid, and examined in a 200 mm. tube in 99.8 per cent. methyl alcoholic solution; volume = 25 c.c.

Exp. V. 0.6 gram.  $\alpha + 5'$ .  $[\alpha]_D + 1.7^\circ$ .

A portion of this sample was then fractionally crystallised from methyl alcohol; it was thus separated into three fractions and a mother liquor, which, however, did not contain a large quantity of the salt.

The whole of each of the three fractions was then separately dissolved in 99.8 per cent. methyl alcohol and examined in a 200 mm. tube; volume of solution = 25 c.c. in each case. The results were as follows:

			$\alpha$ .	$[\alpha]_D$ .
Exp. VI	1st fraction	0.3170 gram	28'	+18.5°
" VII	2nd "	0.4510 "	+12'	+ 5.5°
" VIII	3rd "	0.3875 "	+23'	+12.3°

These three fractions and the parent substance (Exp. V) all melted sharply and simultaneously at about 193°, and yet there is a great difference in their specific rotations; moreover, the

specific rotation of all three fractions is very much higher than that of the parent substance.

In the course of these experiments, there seemed to be indications of the occurrence of mutarotation, the first readings sometimes showing a smaller dextrorotation than the later ones; for this reason, the observations in Exps. VI to VIII were not taken until some time after the solutions had been prepared, but in the case of Exps. I and V no particular attention was paid to this matter as mutarotation had not been suspected.

*Mutarotation of the  $\alpha$ -Salt.*

In order to study this supposed mutarotation and, if possible, to obtain some fairly concordant values for the specific rotation of the  $\alpha$ -salt, a considerable quantity of a fresh sample was obtained by repeated crystallisation from methyl alcohol; this sample was then separated by further crystallisation from methyl alcohol into three fractions, a very small quantity only being left in the mother liquor. All the crystallisations were carried out as quickly as possible, the first and second deposits being obtained by merely cooling the alcoholic solution, and the third by cooling after rapidly boiling off some of the solvent.

The three fractions and the parent substance all melted sharply and simultaneously at  $193^{\circ}$ , and the residue from the mother liquor sintered only a few degrees lower, namely, at about  $188^{\circ}$ .

The samples were dried for a few minutes at  $100^{\circ}$ , and then over sulphuric acid.

For the determination of the specific rotation, 99.8 per cent. methyl alcohol was again employed, the volume being 25 c.c. and the column of liquid 200 mm.

				$\alpha$	$[\alpha]_D$
Exp. IX.	Fraction I.	0.3 gram.	$\left\{ \begin{matrix} (i) \\ (f) \end{matrix} \right.$	$+27^{\circ}.0$ $36^{\circ}.5$	$+18^{\circ}.7$ $25.4$
,,	X.	,, II.	0.3 ,, $\left\{ \begin{matrix} (i) \\ (f) \end{matrix} \right.$	$17^{\circ}.7$ $29^{\circ}.7$	$12.3$ $20.6$
				$31^{\circ}.7$	$22.1$
,,	XI.	,, III.	0.3. ,, $\left\{ \begin{matrix} (i) \\ (f) \end{matrix} \right.$	$15^{\circ}.8$ $36^{\circ}.0$	$11.0$ $25.0$

The mean of the first 6—8 readings, taken as soon as possible after dissolving the salt, gives the value for what may be considered to be approximately the initial specific rotation. These values are given first, under (i), but as the rotation increases in the course of a few minutes, it is not possible to determine them very accurately. After about an hour's time, or less, the rotation apparently becomes

constant, and the average of the readings then taken gives the final value ( $f$ ).

It is obvious from these results that the  $\alpha$ -salt shows mutarotation in methyl alcoholic solution in a very marked manner, the initial value for the specific rotation being less than half the final value in Exp. XI. The agreement between the final results obtained with the three different fractions, considering the large experimental error, is also fairly satisfactory, and might be taken as an indication that the  $\alpha$ -salt is a stable and homogeneous substance.

In order to check these results and study more closely this change in specific rotation, the following experiments were next made.

A sample of  $\alpha$ -salt which, judging by its melting point, was free from its isomeride, was crystallised three times from hot ethyl alcohol; the most sparingly soluble portion and two successive deposits from the mother liquors all seemed to be pure  $\alpha$ -salt.

The most sparingly soluble portion was then examined in 99.8 per cent. methyl alcoholic solution in a 200 mm. tube, 0.3 gram of the salt being used, and the volume of the solution 25 c.c.

Exp. XII.—The average of the first seven readings, which ranged from  $\alpha + 3'$  to  $+11'$ , and which rose almost continuously, gave

$$\alpha + 7' \qquad [a]_D + 4.8^\circ$$

This is a much lower result than any of the initial values given before, perhaps owing to the fact that the salt was very finely divided and dissolved very quickly, so that all the readings were taken within less than 5 minutes after pouring the alcohol on to the salt.

The average of six readings taken about 15 minutes later gave

$$\alpha + 25' \qquad [a]_D + 17.3^\circ$$

Thirty minutes later still, that is to say, about 50 minutes after solution commenced, the average of six readings gave

$$\alpha + 34' \qquad [a]_D + 23.6^\circ$$

The solution was then left in the polarimeter tube overnight and examined the next morning, when the average reading was

$$\alpha + 30' \qquad [a]_D + 20.8^\circ$$

After a further lapse of 24 hours, the average reading was again

$$\alpha + 30' \qquad [a]_D + 20.8^\circ$$

The value  $[a]_D + 23.6^\circ$  compares well with the results obtained in Exps. IX to XI, and the difference between it and the last result,



$[\alpha]_D + 20.8^\circ$ , is practically within the limits of experimental error, as changes of temperature no doubt occurred.

A consideration of the results recorded in Exps. I to XII would, perhaps, lead to the conclusion that, in spite of the statement on p. 913, the observations in Exps. VI to VIII had been taken before mutarotation had ceased. Such a view would, of course, explain in a great measure the differences in the observed values for the specific rotation of the  $\alpha$ -salt. Fortunately, an opportunity occurred to set all such doubts at rest, as will be seen from the results of the following experiments.

A sample of the  $\alpha$ -salt, prepared directly from the acid by evaporating the latter with an aqueous solution of externally compensated base, and then fractionally crystallising from ethyl alcohol, was finally obtained in a very fine state of division and was dried over sulphuric acid; this sample melted almost sharply at about  $193^\circ$ , and showed no sign of sintering even at  $190^\circ$ .

Exp. XIII. 0.4 gram of this sample was then dissolved in 99.8 per cent. methyl alcohol, the solution diluted to 25 c.c. and examined in a 200 mm. tube.

The average of the first seven readings taken in less than 5 minutes after first adding the solvent was

$$\alpha - 15' \qquad [\alpha]_D - 7.8^\circ$$

The solution was left in the tube and examined 15 minutes, 30 minutes, and 15 hours later, but no appreciable change in rotation was observed, the greatest difference between the average readings taken at the four different times being only about  $4'$ , when at the end of 15 hours the specific rotation had apparently become  $[\alpha]_D - 5.7^\circ$ . This difference is so small that it may be neglected.

The melting point of the original sample was again taken, and also that of the deposit obtained on evaporating practically to dryness the solution of the salt used in this experiment; the two specimens melted sharply and simultaneously at about  $193^\circ$ , and the deposit from the methyl alcoholic solution appeared to be a pure homogeneous compound.

It is thus proved conclusively that different samples of the  $\alpha$ -salt, all melting at the same temperature and apparently pure, may have a specific rotation  $[\alpha]_D$  ranging from about  $-8^\circ$  to  $+25^\circ$ , and that these widely different values are obtained even when sufficient time has been allowed for the ordinary mutarotation of the salt to have taken place.

Now it has been observed by Lowry, by whom the term mutarotation was first employed in connection with such changes (Trans., 1899, 75, 211), that chloroform solutions of nitrocamphor which ordinarily

exhibit the phenomenon of mutarotation, sometimes fail to do so spontaneously and remain unchanged during several days; but that when such labile solutions are disturbed or warmed, mutarotation sets in and takes its normal course.

In order to ascertain whether anything of this kind occurred in the case of the  $\alpha$ -salt, the methyl alcoholic solution of the salt used in Exp. XIII was kept for some days, then heated for some time on the water-bath and after cooling, diluted to its original volume; on examination, it was found to show the same rotation as before, namely,  $[\alpha]_D -7^\circ$ .

It may be concluded from this result that the different values obtained for the specific rotation of the  $\alpha$ -salt cannot be attributed to the non-occurrence or only partial occurrence of mutarotation; the question arises then what other explanation can be advanced?

A satisfactory answer to this question, and to another, namely, what is the cause of the mutarotation of the  $\alpha$ -salt, cannot be given; the second point, however, will be considered later on, when the results of the examination of the  $\beta$ -salt have been described.

#### *Specific Rotation of the $\beta$ -Salt.*

The first samples of the  $\beta$ -salt of hydrindamine and *cis*- $\pi$ -camphanic acid which were examined optically, did not give very concordant results, but the values for the specific rotation which were obtained with different preparations were not so widely different as in the case of those of the  $\alpha$ -salt.

The samples used in these experiments were all dried over sulphuric acid, but sometimes they were previously heated for a few minutes on a water-oven in order to expel adherent alcohol or ether. The determinations were all made with a 200 mm. tube, and in the following experiments the given weight of substance was dissolved in 99.8 per cent. methyl alcohol, the solution being diluted to 25 c.c.

Exp. XIV.	0.2970 gram	$\alpha - 15'$	$[\alpha]_D - 10.3^\circ$
Exp. XV.	0.3     ,,	$\alpha - 13'$	$[\alpha]_D - 9.0^\circ$
Exp. XVI.	0.6     ,,	$\alpha - 30.5'$	$[\alpha]_D - 10.6^\circ$

The following determinations were made in ethyl alcohol (98 per cent.) solution, all other conditions remaining unchanged:

Exp. XVII.	0.3 gram	$\alpha - 9'$	$[\alpha]_D - 6.2^\circ$
Exp. XVIII.	0.3     ,,	$\alpha - 14'$	$[\alpha]_D - 9.7^\circ$

All the samples used above melted almost sharply at about  $173^\circ$ , and they were all different preparations, the last two results being obtained with successive fractions from one series of crystallisations.

As the experimental error in all these determinations is rather

large owing to the very feeble rotation, the above results might have been taken to be sufficiently concordant; but in the light of the experience gained in studying the  $\alpha$ -salt, it seemed possible that the values actually obtained might not represent the true specific rotation of the  $\beta$ -salt.

In order, therefore, to further test the value of the above results, a considerable quantity of a fresh sample of the  $\beta$ -salt was prepared; this sample, judged by its melting point, was free from the isomeride, and had the specific rotation  $[\alpha]_D - 15.2^\circ$  when examined in methyl alcohol in a 200 mm. tube; volume of solution, 25 c.c.

Exp. XIX. 0.3 gram.  $\alpha - 22'$ .  $[\alpha]_D - 15.2^\circ$ .

This sample was then fractionally crystallised from methyl alcohol in such a way that a small quantity (about 15 per cent. of the whole) of the most sparingly soluble portion was separated; the remainder was obtained in two fractions, which were separately examined in methyl alcoholic solution in a 200 mm. tube; volume of solution, 25 c.c.

Exp. XX. Fraction I. 0.242 gram  $\alpha - 13'$   $[\alpha]_D - 11.2^\circ$

Exp. XXI. „ II. 0.3 „  $\alpha - 23'$   $[\alpha]_D - 16.0^\circ$

In these experiments, not only was the specific rotation of the original sample found to be considerably higher than that of any previous preparation, but there were also indications that the sample had been resolved into dissimilar parts on fractional crystallisation.

The next attempt to obtain a constant value for the specific rotation of the  $\beta$ -salt was made in the following manner. A sample, melting at  $173^\circ$ , which had been very carefully prepared, was dissolved in hot ethyl alcohol; by merely cooling the solution, separating consecutive deposits, and then precipitating with ether as completely as possible, this sample was separated into three fractions, which are numbered in the order in which they were obtained. Their specific rotations were then determined in methyl alcoholic solution in a 200 mm. tube, the volume of the solution being 25 c.c.

Exp. XXII. Fraction I. { 0.3 gram  $\alpha - 20'$   $[\alpha]_D - 13.8^\circ$   
0.6 „  $\alpha - 44$   $[\alpha]_D - 15.2^\circ$

Exp. XXIII. „ II. 0.3 „  $\alpha - 30'$   $[\alpha]_D - 20.8^\circ$

Exp. XXIV. „ III. 0.3 „  $\alpha - 29'$   $[\alpha]_D - 20.0^\circ$

In spite of the considerable difference between their specific rotations, the fractions I and II melted simultaneously at  $173^\circ$ , and the presence of  $\alpha$ -salt in the former could not be detected; the sample of salt recovered on evaporating the methyl alcoholic solutions which were used for these determinations also melted at the same temperature as before, and simultaneously with the original preparation.

As this method of rapid crystallisation had given two consecutive fractions having the same specific rotation, and also a value which was considerably higher than that of any previous preparation, it seemed that a repetition of this process was all that was necessary in order to finally determine the specific rotation of the  $\beta$ -salt.

Accordingly, a fresh sample of carefully recrystallised  $\beta$ -salt was prepared; it melted sharply at  $173^{\circ}$ , and had the specific rotation  $[\alpha]_D - 13.3$  (see below, Exp. XXV). It was dissolved in hot ethyl alcohol, and then by cooling, and finally by adding ether to the solution, the sample was separated into three successive fractions, which are numbered in the order in which they were deposited. The specific rotation of the original sample and of the three fractions was then determined in ethyl alcoholic solution in a 200 mm. tube, the volume of the liquid being 25 c.c. in all cases:

Exp. XXV.	Original sample.	0.3 gram	$\alpha - 19'$	$[\alpha]_D - 13.3^{\circ}$
	Fraction I.	0.3 "	$\alpha - 15'$	$[\alpha]_D - 10.4^{\circ}$
	" II.	0.3 "	$\alpha - 15'$	$[\alpha]_D - 10.4^{\circ}$
	" III.	0.3 "	$\alpha - 15'$	$[\alpha]_D - 10.4^{\circ}$

These results differ entirely from those obtained in the last series of fractional crystallisations, and the most soluble portions have now the same specific rotation as the first deposit. All these, as well as all previous examples, had the same melting point, and yet the specific rotation ranges from about  $-10^{\circ}$  to  $-20^{\circ}$ .

The following explanation of these results may be suggested. In the first place, it is not impossible that even when the  $\beta$ -salt shows its normal melting point, it may nevertheless contain a small proportion of the  $\alpha$ -isomeride. When a sample of the  $\beta$ -salt melting at  $173^{\circ}$  is intimately mixed with an approximately equal quantity of the  $\alpha$ -salt, there certainly results a mixture which has a very indefinite melting point, and which does not liquefy completely until about  $180^{\circ}$ , but it is quite possible that the samples supposed to be  $\beta$ -salt already contain variable quantities of the  $\alpha$ -isomeride, and that the melting point is not appreciably altered by a small change in the quantity of the latter; as already stated, the melting point of the  $\beta$ -salt is not very sharp, and although so many preparations have been found to melt at this constant temperature, it is not thereby proved that the  $\alpha$ -isomeride is altogether absent.

The difficulty of obtaining samples of the  $\beta$ -salt free from its isomeride may, in its turn, be due to conversion of a little of the former into the latter during crystallisation; although it is true that the sample recovered on evaporating a dilute solution in ethyl or methyl alcohol has the same melting point as before, it does not necessarily follow that no change has occurred during this process;

repeated evaporation with alcohol, as already stated, does bring about the conversion of the  $\beta$ -salt into the  $\alpha$ -isomeride to some extent, and this change takes place in a greater degree on evaporating an aqueous solution only once.

In the case of the  $\alpha$ -salt, similar explanations of the much greater difference in the specific rotations of different samples could not be considered as in any way probable, and it is possible, therefore, that the difficulty of obtaining a constant specific rotation may be due to the same cause in both cases.

*Mutarotation, not shown by the  $\beta$ -Salt.*

Before passing on to describe the results of the optical examination of the  $\alpha$ - and  $\beta$ -salts in aqueous solution, attention may be drawn to one important difference in the behaviour of the two isomerides, namely, that the latter, unlike the former, does not show any definite sign of mutarotation. Although many solutions of the  $\beta$ -salt have been examined, observations taken as soon as possible after solution gave essentially the same results as those taken after the lapse of several hours or even days: only in one case, namely, in that of Exp. XXII, were even faint indications of mutarotation observable. The average of the first eight readings in the first determination made with this sample gave  $[\alpha]_D -9.3^\circ$ , whilst the average of ten readings taken about two hours afterwards gave  $[\alpha]_D -13.8^\circ$ ; in the second determination, however, using the same sample and a solution containing twice as much salt, the average of the readings taken as quickly as possible, was the same as that of those taken the next day. As the difference in the one case just referred to is almost within the limits of experimental error, it must be concluded either that the  $\beta$ -salt does not show mutarotation at all, or that the change takes place so quickly that it cannot be followed experimentally. Considering the close relationship between the two isomerides, it is difficult to say which alternative is to be preferred.

The cause of the mutarotation in the case of the  $\alpha$ -salt is not apparent; it is very improbable, in fact almost impossible, that it could be due to the hydrolysis of the lactone ring in alcoholic solution, for the following reasons:—The  $\alpha$ -salt does not combine with another molecule of hydrindamine, even when it is heated with a solution containing excess of that base; solutions of the acid itself do not show mutarotation in methyl alcoholic solution; solutions of ammonium *cis*- $\pi$ -camphanate containing free ammonia do not show mutarotation, and this is also true of the piperidine salt in presence of free piperidine.

It is also improbable that the change in rotation is due to the

hydration of the base in any way, because, if this were so, the  $\beta$ -salt should behave in a similar manner; that is to say, the change should take place with approximately the same rapidity, and thus be capable of experimental verification.

The phenomenon of mutarotation, however, being still obscure, even in the case of compounds of known constitution, it would not be justifiable to conclude that because the  $\beta$ -salt does not behave similarly to the  $\alpha$ -salt in this respect, it must necessarily differ from the latter in constitution.

### *Specific Rotation in Aqueous Solution.*

Although it did not seem very probable that the hydrindamine salts of *cis*- $\pi$ -camphanic acid would be dissociated in dilute aqueous solution to a sufficient extent to give molecular rotations comparable with those of other salts of this acid, it seemed interesting to examine them optically under these conditions, partly for purposes of comparison, partly in order to try and follow polarimetrically the conversion of one into the other, which, for the reasons already stated, doubtless takes place. That this conversion would probably take place most rapidly in dilute aqueous solution is, perhaps, a proposition which admits of some discussion; for when the salts are electrolytically dissociated, they are, according to the author's views, no longer capable of being converted one into the other, and it would therefore depend on the amount of this dissociation, as well as on the extent of hydrolytic dissociation, whether the transformation of one isomeride into the other could take place at all, and, if so, the rate at which it would occur.

The following experiments were made, in order to obtain information on these points.

*$\alpha$ -Salt.*—A sample of the  $\alpha$ -salt, melting at the right temperature, was recrystallised from alcohol and dried over sulphuric acid; 0.25 gram, dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave

$$\alpha - 20' \quad [\alpha]_D - 16.7^\circ.$$

The wide differences shown by different preparations of the  $\alpha$ -salt in methyl alcoholic solution made it necessary to confirm this result, and a second determination was therefore made with a specimen obtained by recrystallising the sample just used three times from ethyl alcohol; 0.25 gram was dissolved, the other conditions remaining the same.

$$\alpha - 19' \quad [\alpha]_D - 15.8^\circ.$$

The specific rotation of this last specimen in methyl alcoholic solution,  $+20.8^\circ$  at its maximum, so that the results of the last two determinations in aqueous solution may be accepted.

It may be mentioned that the  $\alpha$ -salt did not show mutarotation in aqueous solution; the average of the readings taken as soon as possible was practically identical with that of observations made 1 hour later, and no change in rotation occurred, even on keeping the aqueous solution at the ordinary temperature during 4 days; this fact does not warrant any conclusion as to the stability of the  $\alpha$ -salt in aqueous solution, as will be seen from the data obtained in the case of the  $\beta$ -salt.

*$\beta$ -Salt.*—The specific rotation of this salt in aqueous solution was determined with the aid of two different preparations, which, however, had both the same specific rotation,  $-10.6^\circ$  in methyl alcoholic solution; both samples had the melting point of the  $\beta$ -salt.

0.25 gram dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave

$$\alpha - 18' \quad [\alpha]_D - 15^\circ.$$

On keeping the solution at the ordinary temperature, no appreciable change in rotation took place in the course of 4 or 5 days, but on then evaporating the solution and allowing to crystallise, the deposit did not fuse at the melting point of the  $\beta$ -salt, but sintered at about  $168^\circ$ , and was not completely liquefied until the temperature had risen to about  $178^\circ$ .

0.6 gram dissolved in water, examined under the same conditions as in the last experiment, gave

$$\alpha - 46' \quad [\alpha]_D - 15.9^\circ.$$

These results are not only sufficiently concordant to be accepted as correct, but are also practically identical with those obtained in the case of the  $\alpha$ -salt.

This last fact, of course, rendered it impossible to ascertain by optical examination whether any conversion of one isomeride into the other took place on keeping their dilute aqueous solutions at the ordinary temperature, but that the identity of their specific rotations is not due to the two isomerides becoming identical in aqueous solution seems to be proved by the further fact that even solutions which have been kept for some time do not yield, on evaporation, products having the same, or even approximately the same, melting point, although both appear to be mixtures. The identity of their specific rotations in aqueous solution may, however, be taken as further evidence of the optical inactivity of the basic components of the two salts.

#### *Molecular Rotations of the Isomeric Salts.*

In the case of the hydrindamine bromo- and chloro-camphorsulphonates, it was possible to compare their molecular rotations with

those of the acid and of other salts, and the results thus obtained have already been discussed. In order to make a similar comparison in the case of the salts of *cis*- $\pi$ -camphanic acid, it was first necessary to determine the molecular rotation of the acid by an examination of its salts with optically inactive bases.

In the first place, the acid itself was examined in order to ascertain whether it showed mutarotation in methyl alcoholic solution comparable with that exhibited by the  $\alpha$ -salt.

0.5 gram of very finely divided acid was dissolved in methyl alcohol (99.8 per cent.), the solution diluted to 25 c.c., and examined as quickly as possible in a 200 mm. tube; the average of eight concordant readings gave:

$$\alpha - 25' \quad [\alpha]_D - 10.5.$$

The same solution, examined about 24 hours later, gave:

$$\alpha - 27' \quad [\alpha]_D - 11.3^\circ,$$

and 24 hours later still, practically the same result was obtained; as the initial and final values are the same within the limits of experimental error, it must be concluded that the acid does not show mutarotation under these conditions.

The acid being almost insoluble in water, the determination of its molecular rotation was made in dilute aqueous ammonia and in dilute aqueous solutions of other bases comparable to hydrindamine.

0.25 gram of the acid was dissolved in water, with the addition of a few drops of ammonia, the solution diluted to 25 c.c., and examined in a 200 mm. tube; the average reading was  $\alpha - 29'$ , from which

$$[\alpha]_D - 24.1^\circ \quad [M]_D - 48.$$

The addition of more ammonia to the solution had no appreciable effect on the specific rotation.

*Piperidine cis- $\pi$ -Camphanate.*—0.25 gram of this salt was examined in aqueous solution; volume, 25 c.c.; tube, 200 mm.

$$\alpha - 24' \quad [\alpha]_D - 20^\circ \quad [M]_D - 56.$$

*Benzylamine cis- $\pi$ -Camphanate.*—This salt was not isolated for the purpose, but a solution of 0.5 gram of the acid in water and a little benzylamine was diluted to 25 c.c., and examined in a 200 mm. tube; the specific and molecular rotations are calculated for the acid.

$$\alpha - 1^\circ 6' \quad [\alpha]_D 27.5^\circ \quad [M]_D - 54.4.$$

These results are not very concordant, but the large experimental error, and the probability that the ammonium, piperidine, and benzylamine salts are only very partially dissociated, have to be taken into consideration.



The specific rotations of the hydrindamine *cis*- $\pi$ -camphanates in aqueous solution being practically identical, and equal to  $-16^\circ$ , their molecular rotations are  $-53^\circ$ , a value which is practically the average of those obtained in the case of the three salts just examined. This agreement is sufficiently close to be taken as confirmatory evidence of the view that the isomeric hydrindamine *cis*- $\pi$ -camphanates are both partially racemic salts.

Mr. Harold Hall, A.I.C., has ably assisted in the preparation and analysis of the salts described in this paper, and the author wishes to express his thanks for the valuable help which he has received.

Part of the cost of the materials used in this investigation has been defrayed by the aid of a Government Grant, and it is the author's pleasant duty to express his gratitude to the Government Grant Committee of the Royal Society for the pecuniary assistance thus afforded him.

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NOTTINGHAM.

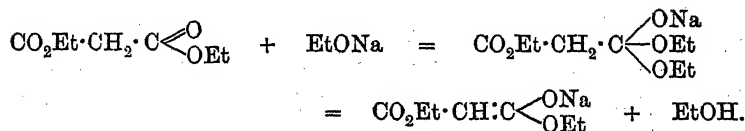
# LXXXI.—*Constitution of Ethyl Sodiocyanacetate and of Ethyl Sodiomethylcyanacetate.*

By JOCELYN FIELD THORPE.

THERE has been considerable discussion from time to time as to the position of the sodium atom in compounds of the type of ethyl malonate.

The property possessed by these compounds of reacting with sodium ethoxide to form sodium derivatives was first observed by Conrad (*Annalen*, 1880, 204, 127), and was ascribed by him to the presence of hydrogen atoms rendered acid by two adjacent electronegative groups, the formula which was for many years accepted without opposition for the sodium derivative of ethyl malonate being  $\text{CHNa}(\text{CO}_2\text{Et})_2$ .

Some time ago, however, Michael (*J. pr. Chem.*, 1888, [ii], 37, 496; 1892, 46, 194) and Nef (*Annalen*, 1891, 266, 67, 113; 1892, 270, 330) called in question the correctness of this formula, and contended that the sodium was not directly combined with the carbon atom, that an oxygen atom intervened, and that the sodium derivative was formed first by the addition of sodium ethoxide, and then by the elimination of the elements of alcohol, thus:



The object of the present paper is not to discuss the formula of ethyl malonate, but to show that all the reactions of ethyl sodiocyanacetate and ethyl sodiomethylcyanacetate seem to indicate that these substances have formulæ similar to that suggested by Michael and by Nef for ethyl malonate.

Perhaps the most noticeable difference between the sodium derivative of ethyl malonate and of ethyl cyanacetate is the ready manner in which the latter is precipitated on adding ethyl cyanacetate to a solution of sodium ethoxide in alcohol. The heavy, white, crystalline precipitate which is then formed can be collected by filtration and recrystallised from alcohol without in any way undergoing decomposition.

The sodium compound of ethyl malonate is precipitated under the same conditions only after long standing in the cold, and cannot be purified by recrystallisation from alcohol; it is furthermore deliquescent and absorbs moisture from damp air, whereas ethyl sodiocyanacetate can be exposed to the air of the laboratory for a considerable period without undergoing change.

Ethyl sodiomalonate on solution in water decomposes into sodium hydroxide and ethyl malonate, the solution showing naturally a strongly alkaline reaction. Ethyl sodiocyanacetate dissolves instantly in water to a clear solution showing only a neutral reaction.

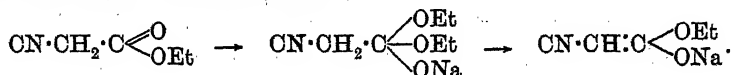
The difference in the behaviour of ethyl sodiocyanacetate and ethyl sodiomalonate on condensation in alcoholic solution with ethyl esters of the acrylic series has been alluded to in a previous communication (Trans., 1899, 75, 49). The yield obtained on condensing these unsaturated esters with ethyl sodiomalonate is frequently so small as to render further investigation of the product impossible (*ibid.*, 52; Auwers, *Ber.*, 1895, 28, 1130), but in no case has ethyl sodiocyanacetate in the same class of condensations given a less yield than 60 per cent. of the theoretical, whilst in many instances as much as 80 per cent. of the theoretical has been obtained. Unlike the derivative obtained from ethyl malonate under similar conditions, this condensation product does not consist of the ethyl ester, but for the most part of an ethyl hydrogen salt of the type  $\text{CO}_2\text{H}\cdot\text{CH}(\text{CN})\cdot\text{CR}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , the relative proportion of ester to acid salt being dependent upon the conditions of the experiment, thus in ethyl alcoholic solution the condensation product, after heating for 12 hours on the water-bath, consists of about 70 per cent. of ethyl hydrogen salt, whereas after 24 hours heating about equal quantities of this and the ester are obtained, and after 36 hours heating, the greater part of the product consists of the ester. Prolonged heating, therefore, decreases the quantity of ethyl hydrogen salt, a fact which does not seem to show that its formation is due to hydrolysis caused by any excess of sodium ethoxide which

The position of the carboxyl group in the ethyl hydrogen salt is shown by its behaviour on distillation, the salt being converted into a nitrile of the type  $\text{CN} \cdot \text{CH}_2 \cdot \text{CR}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , which, on hydrolysis, yields the corresponding acid,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CR}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

A number of these condensations has been studied, and a detailed account of them will be found in the following papers.

The abnormal behaviour of ethyl sodiocyanacetate led to a study of the properties and reactions of this compound and of the corresponding sodium derivative of ethyl methylcyanacetate, with the results which form the subject of these communications.

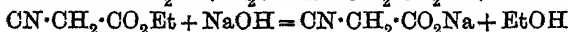
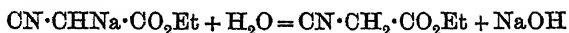
For the reasons which follow, it would seem that the formula which will best explain the reactions of these substances is  $\text{CN} \cdot \text{CR} : \text{C} \begin{smallmatrix} \text{ONa} \\ \text{OEt} \end{smallmatrix}$ , where R may be either hydrogen or an alkyl group, the compound being formed from the ethyl ester by the addition of sodium ethoxide and elimination of alcohol, thus:



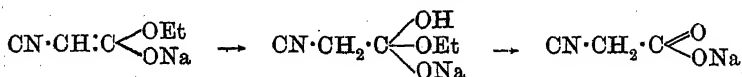
#### *Action of Water on Ethyl Sodiocyanacetate.*

The sodium derivative of ethyl cyanacetate when quite pure dissolves in water to a clear solution, and at no time does the solution show an alkaline reaction, yet on evaporating to dryness in a vacuum over sulphuric acid sodium cyanacetate is obtained; if the ice-cold solution is cautiously acidified, no separation of oil, indicating that ethyl cyanacetate has been regenerated, is observed.

From the equations



it might be expected that the presence of free caustic soda in the solution would be detected, unless, of course, it be supposed that at the moment of its formation it hydrolyses the ethyl ester to the corresponding sodium salt. This, however, is rendered improbable by the fact that ethyl cyanacetate is not readily acted on by cold caustic soda solution, and is only slowly hydrolysed on boiling with this reagent. It therefore seems very probable that the sodium atom in the sodium compound of the ethyl ester is attached to the same carbon atom as it is in the sodium salt of the corresponding acid, and that the action of water can be represented in the following way:



*Formation of Ethyl Hydrogen Salts in the Condensations of Ethyl Sodiocyanacetate with  $\alpha\beta$ -Unsaturated Ethyl Esters.*

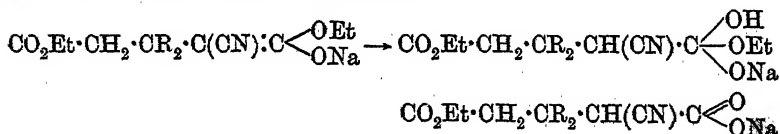
In the condensation of ethyl sodiocyanacetate with unsaturated ethyl esters of the acrylic series in alcoholic solution, the product under suitable conditions consists of a large proportion of ethyl hydrogen salt mixed with the ethyl ester, the former being slowly converted into the latter on prolonging the heating. It was further stated that the carboxyl group is attached to the same carbon atom as the cyano-group. This fact can be readily explained as follows.

The first action of the unsaturated ethyl ester on the sodium compound takes place thus :



where R may be either an alkyl radicle or hydrogen.

On adding water to the compound, the same action takes place as when water is added to ethyl sodiocyanacetate, water being added on and the elements of alcohol eliminated :



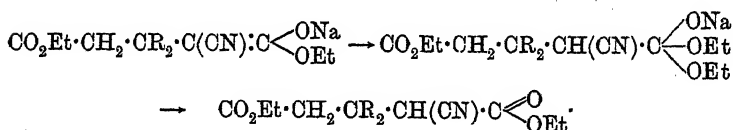
a sodium salt which, on acidifying, would yield the ethyl hydrogen salt.

The unsaturated nature of this sodium compound is difficult to prove conclusively. It is deposited in the condensation mixture as a gelatinous precipitate, which decolorises iodine, yielding a product containing large quantities of this element, but up to the present no means have been devised for obtaining it in a pure condition. Further experiments on this substance, and also on the action of bromine upon the sodium compound, are still in progress.

The formation of ethyl ester, and its production from the ethyl hydrogen salt on prolonging the heating of the alcoholic solution employed in the condensation, can be explained as follows.

Ethyl sodiocyanacetate is produced in its unsaturated form by the addition of sodium ethoxide and splitting off of alcohol, and although there is no tendency for this compound to again take up the elements of alcohol on prolonged boiling with this solvent, yet this seems to happen with more complex unsaturated sodium derivatives, as, for instance, the condensation product mentioned above. As already stated if the heating of the alcoholic solution is prolonged for from ~~one~~ days, hardly a trace of ethyl hydrogen salt is produced, and the

same result is obtained if the mixture is heated in sealed tubes in a salt bath for 24 hours, the product in each case consisting almost entirely of ethyl ester.\* This is most probably due to the addition of alcohol to the unsaturated compound, forming an additive product which on treatment with water would yield the ethyl ester.



The relative proportion of ethyl hydrogen salt to ethyl ester, produced in these reactions, is more clearly seen in cases in which the sodium compound is treated directly with an alkyl iodide, or with a halogen derivative of a fatty ethyl ester.

The method of bringing this about has already been described (Perkin and Thorpe, *Trans.*, 1899, 75, 62, 898),  $\alpha\beta$ -trimethylglutaric acid and the acid represented by von Baeyer's formula for isocamphoric acid having been synthetically prepared in this way. Subsequently, it was found that the alkyl iodide or halogen ethyl ester reacts only with that portion of the condensation product which would have yielded the ethyl hydrogen salt had it been worked up before treatment with the halogen compound. This is proved by the fact that those conditions which yield the largest quantity of the second condensation product yield also an equally large quantity of ethyl hydrogen salt, and that those conditions giving the smallest yield of ethyl hydrogen salt yield also the smallest quantity of the second condensation product.

A good instance of this can be taken in the condensation product obtained by condensing ethyl dimethylacrylate with ethyl sodiocyanacetate, and treating the product with ethyl bromacetate (*Trans.*, 1899, 75, 898). The products in this case boil sufficiently far apart to be readily separated by fractional distillation, and it was found that the proportion of ethyl dimethylcyanobutanetricarboxylate to ethyl dimethyleyanopropanedicarboxylate varied with the conditions employed, and that those conditions which would have yielded the largest quantity of ethyl hydrogen salt, had the condensation mixture been worked up before adding ethyl bromacetate, gave the largest quantity

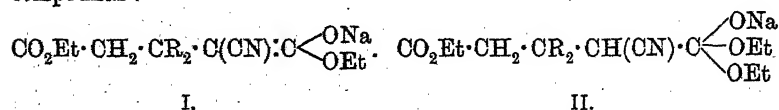
\* The details of an actual experiment may be given. A mixture of 118 grams of ethyl cyanacetate, 129 grams of ethyl dimethylacrylate, and 23 grams of sodium, dissolved in 270 grams of absolute alcohol, gave on heating:

8	hours,	200	grams	ethyl	hydrogen	salt,	10	grams	diethyl	ester.
10	"	118	"	"	"	"	90	"	"	"
20	"	55	"	"	"	"	145	"	"	"
36	"	20	"	"	"	"	175	"	"	"

of ethyl dimethylcyanobutanetricarboxylate after treatment with ethyl bromacetate.

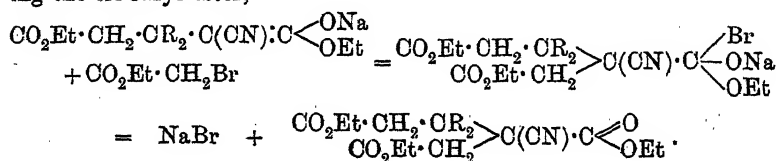
No formation of ethyl hydrogen salt could be observed in any case in which the condensation product had been treated with an alkyl iodide or bromo-ethyl ester.

The product of a condensation between ethyl sodiocyanacetate and an ethyl ester of the acrylic series therefore consists of two sodium compounds:

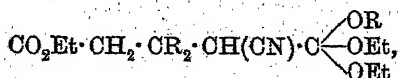


the relative proportion in which they are present being entirely dependent on the conditions of the experiment.

The bromo-ethyl ester then reacts with the sodium derivative I, forming the tri-ethyl ester,

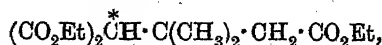


It at first seemed strange that the saturated sodium compound, II, should not react with the halogen compound to form an ortho-derivative of the type

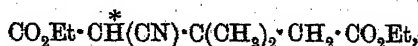


but no compound of this kind could be isolated from the product.

An explanation for this may be found in the fact that compounds of the type  $\frac{\text{X}}{\text{X}} > \text{CH} \cdot \text{CR}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , do not appear to react with sodium ethoxide to form sodium derivatives. Thus it has been found (Perkin and Thorpe, *Trans.*, 1899, 75, 63; Balbiano, private communication) that ethyl dimethylpropanetricarboxylate,

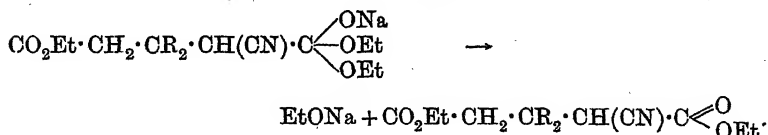


and ethyl dimethylcyanotricarboxylate,



although containing the hydrogen atoms marked (\*) attached to the same carbon atoms as two electronegative groups, do not react with sodium ethoxide to form sodium compounds.

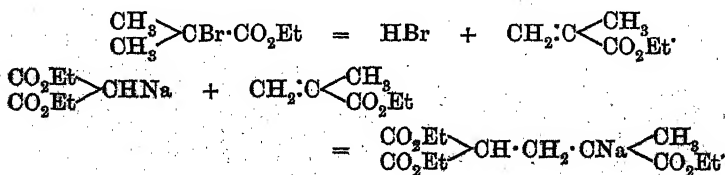
It is therefore highly probable that a sodium derivative of the type II would be an unstable substance, and at the moment of formation would split off sodium ethoxide, and pass into the ethyl ester



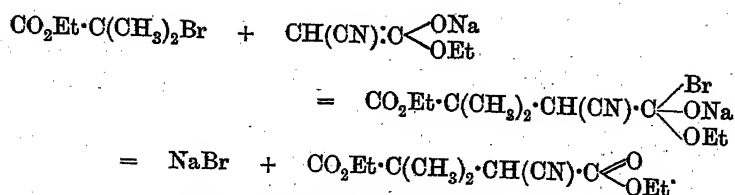
This explanation would further account for the fact frequently noticed in these condensations, namely, that although the original mixture is neutral to litmus when treated with water, yet after prolonged boiling it shows a strongly alkaline reaction.

The assumption of this formula for ethyl sodiocyanacetate might also explain the facts noticed by Bone and Sprankling (*Trans.*, 1899, 75, 845), who found that the condensation of ethyl sodiocyanacetate with some esters of  $\alpha$ -bromo-fatty acids gave almost quantitative yields of the corresponding succinic derivatives, whereas the same condensation carried out with ethyl sodiomalonate yielded mixtures of the glutaric and succinic derivatives.

The formation of glutaric derivatives in such reactions is due, as Auwers showed (Auwers and Koebner, *Ber.*, 1891, 24, 1923; Auwers, Koebner, and von Meyenburg, *ibid.*, 2887), to elimination of hydrogen bromide from the fatty halogen ester, and condensation of the unsaturated ethyl ester thus formed with ethyl sodiomalonate; thus taking as an instance the condensation of ethyl bromisobutyrate with ethyl sodiomalonate, the course of the reaction yielding the glutaric derivative is as follows:

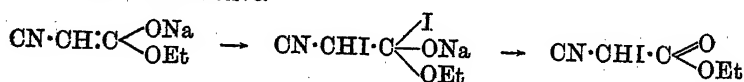


If, however, the ethyl malonate be replaced by ethyl cyanacetate, no trace of the glutaric derivative is obtained, and the product consists entirely of ethyl dimethylcyanoethanetricarboxylate. This difference in behaviour can hardly be due to the difference in solubility of the sodium derivatives of ethyl malonate and ethyl cyanacetate in alcohol, since ethyl sodiocyanacetate, although sparingly soluble in cold, readily dissolves in boiling alcohol, but can be explained on the assumption that the reaction is an additive one:



*Action of Iodine on Ethyl Sodiocyanacetate.*

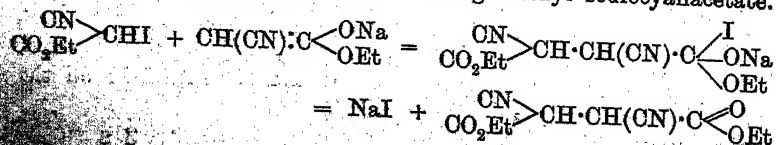
Ethyl sodiocyanacetate forms additive products with bromine and iodine, and does not behave like ethyl sodiomalonate, which is directly transformed into ethyl ethanetetracarboxylate. If excess of iodine in dry ethereal solution is added to the finely ground sodium compound of ethyl cyanacetate suspended in dry ether, and the mixture quickly worked up by adding water and shaking the ethereal solution with sodium carbonate, an oil is obtained containing iodine and giving figures on analysis corresponding with those required for the compound  $\text{CN}\cdot\text{CHI}\cdot\text{CO}_2\text{Et}$ , which is evidently formed by the addition of iodine to the sodium derivative.



The compound decomposes on distillation under diminished pressure, and is therefore difficult to obtain pure.

The sodium derivative does not decolorise the theoretical quantity of iodine required for two equivalents of iodine to one of the compound. By the direct addition of the ethereal solution of iodine, only about 60 per cent. of this amount is decolorised, but by grinding the compound in a mortar in contact with the iodine solution, the amount absorbed is increased to about 80 per cent. of the theoretical quantity; the difficulty is evidently due to the precipitation of sodium iodide on the sodium compound, and the consequent retardation of the reaction. That the remaining 20 per cent. is not absorbed is evidently due to the following reasons. If the product is not very quickly worked up, or if the temperature is allowed to rise during the progress of the reaction, a secondary change takes place, with the ultimate formation of ethyl dicyanosuccinate, which corresponds to ethyl ethanetetracarboxylate formed by the action of iodine on ethyl sodiomalonate.

The formation of this secondary product is caused by the condensation of ethyl iodocyanacetate with unchanged ethyl sodiocyanacetate.





Since this secondary reaction takes place slowly even in ice-cold solutions, the non-absorption of the calculated quantity of iodine is readily understood.

Similar experiments with ethyl sodiomalonate showed no trace of the formation of an additive product containing iodine, and it is therefore hardly likely that the formation of ethyl iodoacyanacetate can be due to the direct replacement of the sodium atom by iodine.

The action of bromine on ethyl sodiocyanacetate shows the formation of the additive product in a still clearer manner, since in this reaction there appears to be no tendency to immediately form the secondary product. The calculated quantity of bromine dissolved in carbon disulphide is readily decolorised by the finely ground sodium compound suspended in carbon disulphide, the product consisting of almost pure ethyl bromocyanacetate,  $\text{CN}\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ , a mobile oil decomposing when distilled under diminished pressure.

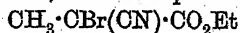
No trace of an additive product containing bromine could be detected in the product formed by the action of bromine on ethyl sodiomalonate. It is interesting to note in connection with this formula for ethyl sodiocyanacetate, that whereas ethyl malonate forms a disodium compound when treated with two equivalents of sodium ethoxide, ethyl cyanacetate under the same conditions forms only a monosodium derivative. The non-formation of a disodium derivative in the case of ethyl cyanacetate may be regarded as a proof in favour of the formula  $\text{CN}\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{ONa} \\ \text{OEt} \end{smallmatrix}$  for the monosodium compound, since this substance could not further react with sodium ethoxide.

#### *Ethyl Sodiomethylcyanacetate.*

The sodium compound of ethyl methylcyanacetate is not precipitated on the addition of alcoholic sodium ethoxide to ethyl methylcyanacetate, and can only be obtained as a gelatinous precipitate on adding a large quantity of dry ether. Since it is readily soluble in alcohol, it cannot, like the sodium compound of ethyl cyanacetate, be recrystallised from this solvent, and hence it was not found possible to prepare it in a condition free from the last traces of sodium ethoxide. Experiments on the action of water on this compound were therefore of no value.

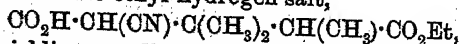
Ethyl sodiomethylcyanacetate, however, combines with iodine to form an additive product, which is a mobile oil decomposing on distillation, and giving on analysis figures corresponding with those required for the compound  $\text{CH}_3\cdot\text{CI}(\text{CN})\cdot\text{CO}_2\text{Et}$ .

By the action of bromine, the corresponding compound



was obtained, although in this case the results were not so satisfactory as with the non-methylated compound.

The yield of condensation product obtained on condensing ethyl sodiomethylcyanacetate with unsaturated ethyl esters is usually very small, and rarely reaches more than 17 per cent. of the theoretical; the product consists, however, of an ethyl hydrogen salt, which behaves in an analogous manner to the ethyl hydrogen salts derived from ethyl cyanacetate. Thus, on condensing ethyl sodiomethylcyanacetate with ethyl dimethylacrylate, about 17 per cent. of the theoretical yield of the ethyl hydrogen salt,

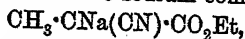


is obtained, yielding on distillation ethyl  $\gamma$ -cyanotrimethylbutyrate,  $\text{CN}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{Et}$ , and this, on hydrolysis, giving  $\alpha\beta$ -trimethylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{H}$ . No trace of diethyl ester could be detected.

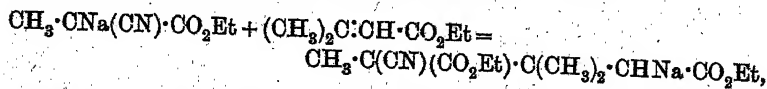
On heating the sodium compound of the condensation product with methyl iodide, a corresponding yield of the methyl derivative is produced, which on hydrolysis and elimination of carbon dioxide is converted into a mixture of the *cis*- and *trans*- $\alpha\alpha_1\beta\beta$ -tetramethylglutaric acids of the formula  $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_3)\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{H}$ .

Evidently, therefore, one of two things must have happened.

(i) Assuming the formula of the sodium compound to be

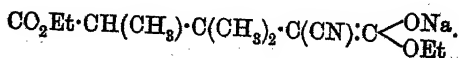
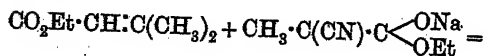


the sodium atom must have changed its position. Thus:



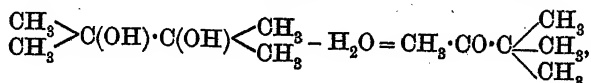
a compound which would yield the tetramethylglutaric acids on methylation, hydrolysis, and elimination of carbon dioxide, or

(ii) Assuming the formula  $\text{CN}\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}\begin{smallmatrix} \text{ONa} \\ \text{OEt} \end{smallmatrix}$  to best express the constitution of the sodium derivative, the methyl group must have changed its position from one carbon atom to another.



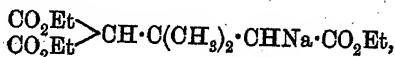
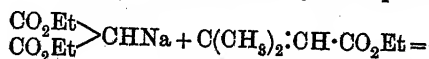
From the similarity in behaviour between ethyl sodiomethylcyanacetate and ethyl sodiocyanacetate, it is probable that the second is the true explanation. It is true that not many instances of a methyl group changing its position from one carbon atom to another are

known in the fatty series, the only case which I can at present call to mind being the conversion of pinacone into pinacolone,\*



but the general reactions of the substance seem to render the assumption necessary, and, as is evident from the smallness of the yield, the change takes place only with much difficulty.

It has been often stated (*Ber.*, 1891, 24, 1923, 2887) that the reaction between ethyl sodiomalonate and unsaturated ethyl esters of the acrylic series is represented by the equation

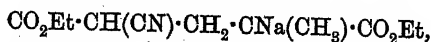


that is to say, that the sodium atom changes its position from one carbon atom to another. If this is actually the case with regard to ethyl sodiocyanacetate, it is a very strong argument against the formula

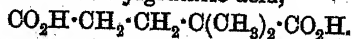
$\text{CN} \cdot \text{CH} : \text{C} \begin{array}{c} \text{ONa} \\ \text{OEt} \end{array}$  for this substance, since a compound of this kind could hardly yield a sodium compound of the type represented in the above equation.

That this view does not represent the true course of the reaction is clearly shown by the following considerations.

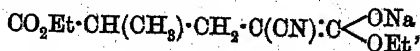
Ethyl  $\alpha$ -methylacrylate,  $\text{CH}_2 \cdot \text{C}(\text{CH}_3) \cdot \text{CO}_2\text{Et}$ , readily condenses with ethyl sodiocyanacetate to form a sodium compound which, according to the equation given above, would have the formula



and would therefore yield, on methylation, hydrolysis, and elimination of carbon dioxide *as-aa*-dimethylglutaric acid,

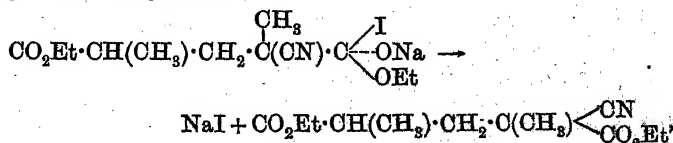


From the alternative formula, on the other hand, the sodium compound would have the constitution



\* It is interesting to note, in connection with the possible wandering of the sodium atom, that ethyl sodiocyanomalonate,  $\text{CN} \cdot \text{CNa}(\text{CO}_2\text{Et})_2$ , which is prepared as Haller (*Ann. Chim. Phys.*, 1889, [vi], 16, 419) showed by the action of ethyl chlorocarbonate on ethyl sodiocyanacetate, does not show the least tendency to combine with unsaturated ethyl esters. In order that condensation should ensue in this case, it would be necessary for either the sodium atom or the carbethoxyl group to change its position. The sodium compound does not decolorise iodine, and is precipitated from its aqueous solutions on the addition of acid as unchanged ethyl cyanomalonate.

giving, with methyl iodide,



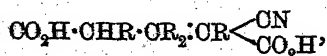
an ethyl ester which, on hydrolysis and elimination of carbon dioxide, would yield the *cis*- and *trans*-forms of symmetrical *aa'*-dimethylglutaric acid.

As a fact, the product consisted, both in this case and in the case of the corresponding reaction with ethyl sodiomalonate, entirely of the *cis*- and *trans-aa'*-dimethylglutaric acids, and no trace of the unsymmetrical compound could be detected. It is therefore certain, apart from the actual formulæ of these sodium compounds, that in these condensations the sodium remains attached to the carbon atom with which it was originally combined.

The *tetramethylglutaric acids*, which have not previously been obtained, are two well-defined substances, behaving as true stereoisomerides; the *cis*-modification melts at 140° and the *trans*-isomeride at 95°, the anhydride of the former is a liquid boiling at 165° under (30 mm.) pressure; the *trans*-acid has no anhydride of its own, but is converted into the anhydride of the *cis*-form on heating in a closed tube at 150° with acetic anhydride; the *cis*-modification is partially converted into the *trans*-isomeride on heating in a sealed tube with concentrated hydrochloric acid at 180°.

In connection with these researches a method was devised by which small quantities of stereoisomeric acids derived from ethyl cyanacetate and its derivatives could be readily separated into their *cis*- and *trans*-modifications. The separation of acids of this type is often a long process, necessitating the use of large quantities of material, and therefore, in the first instance, experiments were tried and the experimental conditions determined by the use of substances which could be obtained in large yields, and would give acids of known constitution. Briefly, the method is as follows.

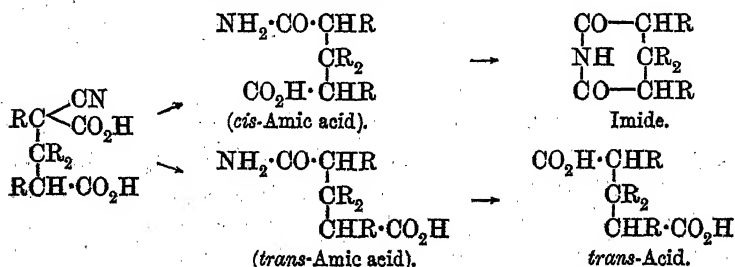
The partial hydrolysis of the cyano-ester formed in these condensations by means of methyl alcoholic potash gives rise to the dibasic cyano-acid,



This is in many cases obtained as a potassium salt readily purified by crystallization and washing with methyl alcohol. On boiling this

potassium salt, or the cyano-acid extracted by means of ether if the potassium salt is soluble in methyl alcohol, with concentrated hydrochloric acid, carbon dioxide is eliminated with the formation of the amic acid, which, like the acids, can exist in *cis*- and *trans*-forms; the process of boiling with hydrochloric acid converts the *cis*-amic acid into the imide, a substance which is not acted on by boiling in hydrochloric acid solution; the *trans*-amic acid, on the other hand, is completely hydrolysed to the *trans*-acid under these conditions.

The process can therefore be represented as follows:



As the imide is insoluble in dilute sodium carbonate solution, the mixture is dissolved in ether and shaken with a solution of sodium carbonate, when the *trans*-acid dissolves, and may be recovered on acidifying and extracting the sodium carbonate washings, whilst the imide remains in the ethereal solution, and can be obtained on evaporation; the imide is converted into the *cis*-acid on hydrolysis with dilute sulphuric acid.

This method, which has so far been applied in three cases, has in each yielded satisfactory results.

These researches were carried out in conjunction with Messrs. Howles, Neale, Udall, and Young, and I beg to thank these gentlemen for the able manner in which they conducted the experiments, a detailed account of which appear in the ensuing papers.

I further wish to thank Prof. W. H. Perkin for many valuable suggestions given during the course of these investigations.

THE OWENS COLLEGE,  
MANCHESTER.

# LXXXII.—cis- and trans- $\alpha,\beta$ -Tetramethylglutaric Acids.

By JOCELYN F. THORPE and WILLIAM J. YOUNG.

*Ethyl Sodiocyanacetate*,  $\text{ON}\cdot\text{CH}_2\text{C}\begin{matrix} \text{ONa} \\ \text{OEt} \end{matrix}$

THE sodium compound of ethyl cyanacetate is precipitated as a white, crystalline powder on adding the calculated quantity of ethyl cyanacetate to an equivalent quantity of sodium dissolved in alcohol. In order to avoid the precipitation of this compound in cakes, which renders subsequent washing difficult, it is advisable to dissolve the ethyl cyanacetate in alcohol and to mix the substances warm; in this way, a fine, granular precipitate can be obtained on cooling the solution. After washing with cold absolute alcohol to remove any excess of sodium ethoxide, the compound is washed with dry ether and placed in a vacuum over sulphuric acid.

Although this process yields the sodium compound sufficiently pure for ordinary purposes, yet it was found extremely difficult to obtain it free from the last traces of sodium ethoxide. This was, however, ultimately effected by recrystallising the substance from hot alcohol, in which it dissolves fairly readily, and from which it separates on cooling. When pure, it does not take up water from the air even after prolonged exposure.

A specimen of the sodium compound thus prepared was analysed with the following result:

0.2415 gave  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 17.01$ .

$\text{C}_5\text{H}_6\text{O}_2\text{NNa}$  requires  $\text{Na} = 17.03$  per cent.

## *Action of Water on Ethyl Sodiocyanacetate.*

Ethyl sodiocyanacetate, free from sodium ethoxide, dissolves in water almost instantly to a clear solution in which no oily drops are visible, and at no time could any free alkali be detected; the solution on boiling still retains its neutral reaction, and on evaporating to dryness a crystalline compound is obtained which gives figures on analysis corresponding to those required for sodium cyanacetate.

0.2357 gave 0.0801  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 10.99$ .

$\text{C}_5\text{H}_6\text{O}_2\text{NNa}$  requires  $\text{Na} = 11.15$  per cent.

On acidifying the solution of the sodium compound in the cold with hydrochloric acid, ethyl cyanacetate is not regenerated.

*Action of Iodine on Ethyl Sodiocyanacetate.*

On adding one equivalent of iodine dissolved in dry ether to one equivalent of the sodium compound suspended in the same solvent, rapid decolorisation ensues, and it was found possible to add 10 per cent. more iodine than was theoretically required before the coloration became permanent. This excess was increased to 80 per cent. on grinding the sodium compound with the iodine solution in a mortar, but beyond this no further absorption of iodine could be brought about.

On rapidly working up the product by adding water, extracting the ethereal layer, and washing the ethereal solution with dilute sodium carbonate solution to remove iodine, an oil remained after removal of the ether which contained large quantities of iodine, and decomposed with evolution of iodine vapour on distillation under reduced pressure. Owing to the fact that it was not found possible to separate it from the product of a secondary reaction, this substance did not yield very satisfactory figures on analysis, the quantity of iodine varying considerably in various experiments. The best results were obtained by quickly adding excess of iodine in ethereal solution to the finely ground sodium compound suspended in ether cooled by means of ice, and immediately adding water; in this way, a substance was obtained which yielded the following figures on analysis:

0.2519 gave 0.2419 AgI.  $I = 52.08$ .

$C_5H_6O_2NI$  requires  $I = 53.18$  per cent.

The secondary reaction mentioned above consists in the further action of the iodo-compound on the unchanged sodium derivative, the product consisting of ethyl dicyanosuccinate, the formation of which depends entirely on the conditions of the experiment.

*Ethyl Dicyanosuccinate*,  $CO_2Et \cdot CH(CN) \cdot CH(CN) \cdot CO_2Et$ , was most conveniently prepared in the following way. The sodium compound (5 grams) was suspended in dry ether, mixed with excess of iodine dissolved in dry ether, and the mixture either allowed to stand for 2 days or heated on the water-bath for 3—4 hours. The product, which was worked up in the way previously described by adding water, separating the ethereal layer, and removing excess of iodine with sodium carbonate solution, yielded a solid residue on removing the ether by evaporation. The ester crystallises from dilute alcohol in lustrous plates and melts at  $120^\circ$ . On analysis:

0.1514 gave 0.2965  $CO_2$  and 0.0756  $H_2O$ .  $C = 53.41$ ;  $H = 5.55$ .

$C_{10}H_{12}O_4N_2$  requires  $C = 53.57$ .  $H = 5.36$  per cent.

Ethyl dicyanosuccinate is a neutral substance which dissolves readily in acetone, alcohol, or ethyl acetate, but is only sparingly soluble in light petroleum, and insoluble in water.

*Action of Bromine on Ethyl Sodiodicyanacetate.*

The action of bromine on the sodium compound is a still more satisfactory indication of its unsaturated nature than the corresponding action of iodine, for in this case there appears to be no tendency to form ethyl dicyanosuccinate, and consequently the additive product with bromine can be obtained in a pure condition.

In this case, the sodium compound was suspended in dried and distilled carbon disulphide, and a solution of bromine dissolved in carbon disulphide added. Rapid decolorisation ensued, and it was found that 10 grams of the sodium compound absorbed 10.3 grams of bromine, the theoretical quantity for two equivalents of bromine to one of the sodium compound being 11.1 grams. From this it would appear that the absorption of bromine is almost complete.

On adding water to the product, separating the layer of carbon disulphide, and washing with water and dilute sodium carbonate solution, an oil remained on evaporation, which decomposed on distillation under reduced pressure, but yet, without further purification, gave the following figures on analysis:

0.2366 gave 0.2328 AgBr. Br = 42.11.

$C_5H_6O_2NBr$  requires Br = 41.66 per cent.

This bromo-derivative is produced to the extent of about 80 per cent. of the theoretical, and a complete study of its properties is in progress.

*Ethyl Sodimethylecyanacetate*,  $CH_3 \cdot C(CN) : C \begin{smallmatrix} \text{ONa} \\ \text{OEt} \end{smallmatrix}$ .

On adding the calculated quantity of ethyl methylecyanacetate to an equivalent quantity of sodium dissolved in alcohol, the sodium compound is not precipitated, but may be obtained in white, flocculent form on adding an excess of dry ether to the mixture. When separated by filtration, washed with dry ether, and dried on a porous plate, it is obtained as a gelatinous solid, which quickly absorbs moisture from the air.

The compound dissolves in water, and the solution exhibits an alkaline reaction, but owing to the difficulty experienced in obtaining it free from sodium ethoxide, it is possible that this alkalinity may be due to traces of the latter, since the only convenient method for purification, namely, solution in alcohol and reprecipitation with ether, would hardly ensure the removal of the last traces of the



*Action of Iodine on Ethyl Methylcyanoacetate.*

In the action of iodine on the sodium compound, as in the action of bromine on ethyl sodiocyanacetate, there appears to be no tendency for any secondary product to be formed. On adding an ethereal solution of iodine to the finely divided sodium compound suspended in dry ether, rapid decolorisation ensues, and on extracting the product in the usual way, it was found to consist of a heavy oil, decomposing on distillation under diminished pressure. On analysis:

0.2136 gave 0.1937 AgI.  $I = 49.01$ .

$C_6H_8O_2NI$  requires  $I = 50.19$  per cent.

No trace of ethyl dimethyldicyanosuccinate could be detected in this product.

The iodo-compound slowly deposits iodine on exposure to sunlight.

*Condensation of Ethyl  $\beta\beta$ -Dimethylacrylate with Ethyl Sodiomethylcyanoacetate.*

This condensation was carried out with the object of determining whether ethyl sodiomethylcyanoacetate condensed with unsaturated ethyl esters in the same manner as ethyl sodiocyanacetate, which, as already stated, yielded a product consisting largely of an ethyl hydrogen salt.

Twenty-three grams of sodium dissolved in alcohol were mixed with 127 grams of ethyl methylcyanoacetate and 128 grams of ethyl dimethylacrylate, the whole being heated on the water-bath for 24 hours. On distilling off the excess of alcohol, adding water, extracting with ether, &c., only unchanged products were obtained on evaporation and fractionation.

On acidifying the mother liquor, an oil separated which, after extraction, was distilled three times under the ordinary pressure, during which process it evolved carbon dioxide and was converted into a mobile oil boiling constantly at  $224^\circ$ . On analysis, numbers were obtained corresponding with those required for *ethyl  $\gamma$ -cyano- $\beta\beta$ -dimethylbutyrate*,  $CN \cdot CH_2 \cdot C(CH_3)_2 \cdot CH(CH_3) \cdot CO_2Et$ .

0.1638 gave 0.3930  $CO_2$  and 0.1374  $H_2O$ .  $C = 65.48$ ;  $H = 9.31$ .

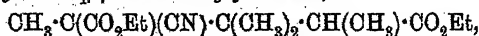
$C_{10}H_{17}O_2N$  requires  $C = 65.57$ ;  $H = 9.29$  per cent.

On hydrolysing this oil with 50 per cent. sulphuric acid, a process requiring from 6—7 hours, and extracting the product, a solid acid was obtained which, after recrystallisation from water, melted at  $87^\circ$ , and was in every respect identical with  *$\alpha\beta\beta$ -trimethylglutaric acid*,  $CO_2H \cdot CH(CH_3) \cdot C(CH_3)_2 \cdot CH_2 \cdot CO_2H$ . The yield of this compound is

only 5 per cent. of that theoretically possible. It is interesting to note, however, that the reaction in this case proceeds in the same way as the corresponding reaction in the case of ethyl cyanacetate. In the present instance, however, no traces of the diethyl ester could be detected.

*Formation of cis- and trans- $\alpha\alpha_1\beta\beta$ -Tetramethylglutaric Acids.*

*Ethyl  $\alpha$ -Cyano- $\alpha\alpha_1\beta\beta$ -tetramethylglutarate,*



is formed to the extent of 17 per cent. of the theoretical yield in the following way. Sodium (dissolved in alcohol) and ethyl methacrylate, in molecular proportion, were mixed with an equivalent quantity of ethyl dimethylacrylate, and heated on the water-bath for 24 hours; excess of methyl iodide was then added, and the heating continued for a further 6 hours. On isolating the product in the usual way, it was found to consist of an oil which distilled at 174–176° under 30 mm. pressure. On analysis:

0.1778 gave 0.4062  $\text{CO}_2$  and 0.1356  $\text{H}_2\text{O}$ .  $\text{C} = 62.32$ ;  $\text{H} = 8.47$ .

$\text{C}_{14}\text{H}_{23}\text{O}_4\text{N}$  requires  $\text{C} = 62.45$ ;  $\text{H} = 8.55$  per cent.

*$\alpha\alpha\beta\beta$ -Tetramethylglutarimide,  $(\text{CH}_3)_2\text{C} \begin{matrix} \text{CH}(\text{CH}_3)\cdot\text{CO} \\ \text{CH}(\text{CH}_3)\cdot\text{CO} \end{matrix} \text{NH}$ .*

Ethyl  $\alpha$ -cyano- $\alpha\alpha_1\beta\beta$ -tetramethylglutarate was first heated on the water-bath for 2 hours with an equal weight of potassium hydroxide, dissolved in methyl alcohol, evaporated several times with water to dryness, and extracted with ether, the oily product being further heated with concentrated hydrochloric acid for one hour.

During this process, vigorous evolution of carbon dioxide occurred, and after extracting with ether and shaking out the ethereal solution three times with dilute sodium carbonate solution, the ether, on evaporation, left a solid residue, which crystallised from water in long, white needles melting at 108°. On analysis:

0.1570 gave 10.9 c.c. nitrogen at 15° and 769 mm.  $\text{N} = 8.34$ .

$\text{C}_9\text{H}_{15}\text{O}_2\text{N}$  requires  $\text{N} = 8.28$  per cent.

The silver salt, prepared by adding a solution of silver nitrate in water to an aqueous solution of the imide to which a few drops of ammonia had been added, is a white, crystalline substance.

0.1114 gave 0.0434 Ag.  $\text{Ag} = 38.91$ .

$\text{C}_9\text{H}_{14}\text{NO}_2\text{Ag}$  requires  $\text{Ag} = 38.95$  per cent.

*cis- $\alpha\alpha'\beta\beta$ -Tetramethylglutaric Acid,*  
 $\text{CH}_3 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H}.$

This acid is obtained by boiling the imide for 2 hours with 50 per cent. sulphuric acid. In this process, a small quantity of the *cis*-acid is converted into the *trans*-isomeride, but the change is not sufficient to prevent the *cis*-acid from being isolated in a pure form by recrystallisation from water, from which it separates in white plates melting at  $140^\circ$ . On analysis:

0.2171 gave 0.4558  $\text{CO}_2$  and 0.1692  $\text{H}_2\text{O}$ .  $\text{C} = 57.25$ ;  $\text{H} = 8.65$ .

$\text{C}_9\text{H}_{16}\text{O}_4$  requires  $\text{C} = 57.44$ ;  $\text{H} = 8.51$  per cent.

The *silver* salt is a white, amorphous precipitate.

0.1673 gave 0.0894 Ag.  $\text{Ag} = 53.44$ .

$\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 53.50$  per cent.

*$\alpha\alpha'\beta\beta$ -Tetramethylglutaric Anhydride*,  $\text{C}_9\text{H}_{14}\text{O}_3$ , is formed by boiling the *cis*-acid with acetyl chloride for 2 hours. It is an oil which does not appear to exist at the ordinary temperature in a crystalline condition; it boils at  $155$ — $158^\circ$  under 30 mm. pressure. On analysis:

0.1957 gave 0.4569  $\text{CO}_2$  and 0.1412  $\text{H}_2\text{O}$ .  $\text{C} = 63.57$ ;  $\text{H} = 8.01$ .

$\text{C}_9\text{H}_{14}\text{O}_3$  requires  $\text{C} = 63.53$ ;  $\text{H} = 8.23$  per cent.

When boiled with water, the anhydride gradually dissolves, and, on cooling, the *cis*-acid, melting at  $140^\circ$ , separates from the solution.

*trans- $\alpha\alpha'\beta\beta$ -Tetramethylglutaric Acid,*  
 $\text{CO}_2\text{H} \cdot \text{CH}(\text{CH}_3) \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H}.$

The *trans*-acid is obtained from the sodium carbonate extracts of the ethereal solution (p. 940) by acidifying, saturating with ammonium sulphate, and extracting with ether. It crystallises from hydrochloric acid in needles, and melts at  $98^\circ$ .

0.1952 gave 0.4105  $\text{CO}_2$  and 0.1514  $\text{H}_2\text{O}$ .  $\text{C} = 57.35$ ;  $\text{H} = 8.61$ .

$\text{C}_9\text{H}_{16}\text{O}_4$  requires  $\text{C} = 57.44$ ;  $\text{H} = 8.51$  per cent.

The *trans*-acid does not yield an anhydride when treated with acetyl chloride, and is recovered unchanged on evaporating the solution.

The *silver* salt is an amorphous powder.

0.1692 gave 0.0910 Ag.  $\text{Ag} = 53.42$ .

$\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 53.50$  per cent.

The *trans*-acid, mixed with *cis*-isomeride, can also be obtained on

hydrolysing the imide with hydrochloric acid in a sealed tube for 6 hours at  $180^{\circ}$ .

The *trans*-acid is converted into the *cis*-isomeride by heating with acetic anhydride in a sealed tube for 5 hours at  $150^{\circ}$ ; on removing the acetic anhydride by evaporation and boiling the residue with water, the *cis*-acid separates on cooling.

*cis*- and *trans*-Tetramethylglutaric acids are therefore quite normal in their behaviour. The fact that the *trans*-acid melted at a lower temperature than the *cis*-isomeride seemed to point to the possibility of the former being a mixture of the two, corresponding to the  $\alpha\alpha_1$ -dimethylglutaric acid, melting at  $103^{\circ}$ , which was long thought to be the *trans*-form, but was subsequently shown to be a mixture of the stereoisomerides. We have seen no reason to doubt the homogeneous character of the acid melting at  $98^{\circ}$ , however, and all attempts to detect the presence of any *cis*-acid in it have been unsuccessful.

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### LXXXIII.— *$\beta$ -Isopropylglutaric Acid and cis- and trans-Methylisopropylglutaric Acids.*

By F. H. HOWLES, JOCELYN F. THORPE, and WILLIAM UDALL.

ETHYL  $\alpha$ -BROMISOBUTYLACETATE is best prepared in the following manner. Isobutylacetic acid, obtained by treating ethyl sodiomalonate with isobutyl bromide, hydrolysing the product after fractionation with ethyl alcoholic potash, and distilling the tribasic acid obtained, is brominated by the Volhard method with phosphorus pentabromide and bromine, and the product poured into absolute alcohol.

The bromo-ester separates as a heavy, yellow oil on pouring the alcoholic solution into water and extracting with ether.

#### *Ethyl $\beta$ -Isopropylacrylate.*

Fifty grams of the bromo-ester without further purification are mixed with 75 grams diethylaniline and boiled on the sand-bath for 9 hours; the solid mass is then treated with hydrochloric acid (1:1) and shaken out with ether, the ethereal solution being washed repeatedly with hydrochloric acid until the last traces of diethylaniline have been washed out; the unsaturated ethyl salt obtained on distilling further boils at  $174^{\circ}$  under 757 mm. pressure.

I. *Condensation of Ethyl  $\beta$ -Isopropylacrylate with Ethyl Sodiocyanacetate.*

Ethyl cyanacetate (19.9 grams) was added to an alcoholic solution of sodium (4 grams) and, after the addition of ethyl  $\beta$ -isopropylacrylate (25 grams), the mixture was heated on the water-bath for 10 hours. On adding the unsaturated ethyl ester, considerable heat was evolved. The product, which consisted of a dark coloured gelatinous solid, was mixed with water and extracted with ether, the ethereal solution giving an oil on evaporation which, on distillation under 30 mm. pressure, gave 13 grams of an oil boiling at  $195^{\circ}$ ; this proved to be *ethyl  $\alpha$ -cyano- $\beta$ -isopropylglutarate*,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CHPr}^s\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ . On analysis:

0.2215 gave 0.4989  $\text{CO}_2$  and 0.1618  $\text{H}_2\text{O}$ .  $\text{C} = 61.43$ ;  $\text{H} = 8.12$ .

$\text{C}_{13}\text{H}_{21}\text{O}_4\text{N}$  requires  $\text{C} = 61.17$ ;  $\text{H} = 8.23$  per cent.

On acidifying the mother liquor, a quantity of oil separated, which after extraction was found to weigh 10 grams. On distillation under ordinary pressure, a vigorous evolution of gas ensued, the liquid after three distillations passing over as a mobile oil boiling at  $234^{\circ}$  under 755 mm. pressure and consisting of *ethyl  $\gamma$ -cyano- $\beta$ -isopropylbutyrate*,  $\text{CN}\cdot\text{CH}_2\cdot\text{CHPr}^s\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ .

0.2113 gave 0.5060  $\text{CO}_2$  and 0.1731  $\text{H}_2\text{O}$ .  $\text{C} = 65.31$ ;  $\text{H} = 9.10$ .

$\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}$  requires  $\text{C} = 65.57$ ;  $\text{H} = 9.29$ .

Another experiment, in which the time of heating was only 3 hours instead of twelve, the same quantities being used, yielded only a trace of diethyl ester, but 30 grams of ethyl hydrogen salt.

*Hydrolysis of the Diethyl Ester.*

On adding an equal weight of potash dissolved in methyl alcohol to the ester, a large quantity of a crystalline potassium salt separated; this was filtered off, washed with methyl alcohol, dissolved in water, and the solution boiled until the last traces of methyl alcohol had been removed. The solution on acidifying, saturating with ammonium sulphate, and extracting with ether, yielded a liquid substance which when boiled for 10 minutes with concentrated hydrochloric acid evolved large quantities of carbon dioxide, and on cooling deposited crystals of  *$\beta$ -isopropylglutarimide*,  $\text{CHPr}^s\cdot\begin{matrix} \text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO} \end{matrix}\cdot\text{NH}$ , this separating from hot water in glistening plates melting at  $120^{\circ}$ .

0.3036 gave 24.2 c.c. nitrogen at  $20^{\circ}$  and 756 mm.  $\text{N} = 9.03$ .

$\text{C}_8\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{N} = 9.07$  per cent.

The *silver* salt is obtained as a white, crystalline precipitate on adding a solution of silver nitrate to a slightly alkaline solution of the imide. On analysis:

0.2913 gave 0.2085 AgBr.  $\text{Ag} = 40.97$ .

$\text{C}_8\text{H}_{12}\text{O}_2\text{NAg}$  requires  $\text{Ag} = 41.13$  per cent.

*$\beta$ -Isopropylglutaric acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHPr}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,

can be prepared either by hydrolysing the pure imide with a 50 per cent. solution of sulphuric acid, the operation usually being finished after heating for 2 hours on the sand-bath, or by heating the imide in a sealed tube with concentrated hydrochloric acid for 6 hours at  $150^\circ$ . In both cases, the acid can be obtained on extracting with ether. It separates from water in needles, and melts at  $100^\circ$ . On analysis:

0.2081 gave 0.4198  $\text{CO}_2$  and 0.1524  $\text{H}_2\text{O}$ .  $\text{C} = 55.02$ ;  $\text{H} = 8.12$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

The *anhydride*,  $\text{CHPr}^\beta\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO}\end{smallmatrix}\right\rangle\text{O}$ , is obtained as a liquid on treating the acid with excess of acetyl chloride for 2 hours on the water-bath. It boils at  $171^\circ$  under 30 mm. pressure.

0.2134 gave 0.4839  $\text{CO}_2$  and 0.1442  $\text{H}_2\text{O}$ .  $\text{C} = 61.85$ ;  $\text{H} = 7.51$ .

$\text{C}_8\text{H}_{10}\text{O}_3$  requires  $\text{C} = 61.54$ ;  $\text{H} = 7.69$  per cent.

*$\beta$ -Isopropylglutaranilic acid*,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPr}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is precipitated when benzene solutions of aniline and the anhydride are mixed together. It crystallises from alcohol in colourless, lustrous plates, melts at  $121^\circ$ , and dissolves in sodium carbonate solution. On analysis:

0.1508 gave 7.5 c.c. nitrogen at  $22^\circ$  and 765 mm.  $\text{N} = 5.68$ .

$\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}$  requires  $\text{N} = 5.62$  per cent.

#### *Action of Methyl Iodide on the Sodium Compound of the Condensation Product.*

Since the object in this case was to produce the methyl derivative, the reaction product was heated for only 3 hours on the water-bath before excess of methyl iodide was gradually added, and the heating continued for 6 hours. On adding water, extracting with ether, and removing the ether by evaporation, a thick, yellow oil remained, which boiled at  $180$ — $183^\circ$  under 19 mm. pressure, and consisted of *ethyl  $\alpha$ -cyano- $\alpha$ -methyl- $\beta$ -isopropylglutarate*,

$\text{CO}_2\text{Et}\cdot\text{C}(\text{CN})(\text{CH}_3)\cdot\text{CHPr}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ .

ANALYSIS:

0.2950 gave 0.6741  $\text{CO}_2$  and 0.2240  $\text{H}_2\text{O}$ .  $\text{C} = 62.33$ ;  $\text{H} = 8.44$ .

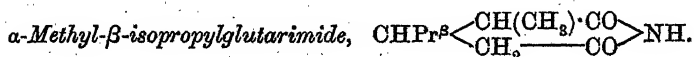
$\text{C}_{14}\text{H}_{23}\text{O}_4\text{N}$  requires  $\text{C} = 62.45$ ;  $\text{H} = 8.55$  per cent.

On adding an equal weight of potash dissolved in methyl alcohol to this ester, hydrolysis at once ensues with evolution of heat, and at the same time a copious precipitation of a crystalline potassium salt takes place. This salt can be separated by filtration and purified by washing with methyl alcohol, when it is obtained as a slightly yellow, crystalline solid, evidently consisting of potassium  $\alpha$ -cyano- $\alpha$ -methyl- $\beta$ -isopropylglutarate.

0.9814 gave 0.6012  $\text{K}_2\text{SO}_4$ .  $\text{K} = 27.46$ .

$\text{C}_{10}\text{H}_{12}\text{O}_4\text{NK}_2$  requires  $\text{K} = 26.99$  per cent.

The salt is extremely soluble in cold water.



On acidifying the concentrated aqueous solution of the potassium salt with hydrochloric acid and extracting with ether, a solid consisting of the dibasic cyano-acid is obtained on evaporation. On boiling this with concentrated hydrochloric acid for 1 hour and again extracting, an ethereal solution of the imide and the *trans*-acid is obtained, which can be freed from the *trans*-acid by shaking with a dilute solution, of sodium carbonate, the imide remaining in the ethereal solution, from which it can be obtained on evaporation. The end point of this reaction, that is to say, the point at which it can be safely assumed that all the *cis*-amic acid formed during the hydrolysis has been converted into imide and all the *trans*-amic acid hydrolysed to *trans*-acid, is usually that point at which the evolution of carbon dioxide ceases.

$\alpha$ -Methyl- $\beta$ -isopropylglutarimide crystallises from water in colourless needles and melts at  $114\text{--}115^\circ$ . On analysis:

0.1438 gave 10.5 c.c. nitrogen at  $14^\circ$  and 765 mm.  $\text{N} = 8.51$ .

$\text{C}_9\text{H}_{15}\text{O}_2\text{N}$  requires  $\text{N} = 8.28$  per cent.

The *silver* salt is precipitated as a white, crystalline powder on adding a solution of silver nitrate to a slightly alkaline solution of the imide. On analysis:

0.3001 gave 0.2042  $\text{AgBr}$ .  $\text{Ag} = 39.10$ .

$\text{C}_9\text{H}_{14}\text{O}_2\text{NAg}$  requires  $\text{Ag} = 39.04$  per cent.

*cis-a-Methyl- $\beta$ -isopropylglutaric Acid,*  
 $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_3)\cdot\text{CHPr}^s\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

The *cis*-acid is best prepared by hydrolysing the imide with 50 per cent. sulphuric acid, the reaction being complete after boiling for 3 hours on the sand-bath. On cooling and extracting with ether, a solid acid remains on evaporation, which separates from hot water in glistening plates melting at  $137^\circ$ . On analysis:

0.1421 gave 0.3001  $\text{CO}_2$  and 0.1080  $\text{H}_2\text{O}$ .  $\text{C} = 57.57$ ;  $\text{H} = 8.44$ .

$\text{C}_9\text{H}_{16}\text{O}_4$  requires  $\text{C} = 57.45$ ;  $\text{H} = 8.51$  per cent.

The *silver* salt is a white amorphous powder.

0.1471 gave 0.0783 Ag.  $\text{Ag} = 53.23$ .

$\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 53.64$  per cent.

The *anhydride*,  $\text{CHPr}^s \begin{array}{c} \text{CH}(\text{CH}_3)\cdot\text{CO} \\ \text{CH}_2\text{---CO} \end{array} \text{O}$ .—On boiling the *cis*-acid with acetyl chloride, it slowly dissolves with evolution of hydrogen chloride, and if the solution is evaporated to dryness after boiling for 1 hour on the water-bath, a solid residue remains. This is insoluble in sodium carbonate solution and crystallises from light petroleum (b. p.  $40\text{--}60^\circ$ ) in glistening plates melting at  $44^\circ$ . On analysis:

0.1445 gave 0.3308  $\text{CO}_2$  and 0.1068  $\text{H}_2\text{O}$ .  $\text{C} = 62.41$ ;  $\text{H} = 8.21$ .

$\text{C}_9\text{H}_{14}\text{O}_3$  requires  $\text{C} = 62.35$ ;  $\text{H} = 8.24$  per cent.

*trans-a-Methyl- $\beta$ -isopropylglutaric acid,*  
 $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_3)\cdot\text{CHPr}^s\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

The solution obtained from the hydrochloric acid hydrolysis by extracting the ethereal extract with sodium carbonate gave a solid acid on acidifying, saturating with ammonium sulphate, extracting with ether, and removing the ether by evaporation. When recrystallised from water, this acid melted at  $101^\circ$ , and at first was thought to be  $\beta$ -isopropylglutaric acid, due to the presence of non-methylated ethyl ester in the product. Its properties, however, were found to be very different from those of  $\beta$ -isopropylglutaric acid, for not only were the crystalline forms of the acids different, but the acid melting at  $101^\circ$  yielded no anhydride on treatment with acetyl chloride, and further, could be completely converted into *cis-a-methyl- $\beta$ -isopropylglutaric anhydride* on heating with acetic anhydride in a closed tube. On analysis:

0.1332 gave 0.2794  $\text{CO}_2$  and 0.1030  $\text{H}_2\text{O}$ .  $\text{C} = 57.25$ ;  $\text{H} = 8.59$ .

0.1878 „ 0.3942  $\text{CO}_2$  „ 0.1437  $\text{H}_2\text{O}$ .  $\text{C} = 57.25$ ;  $\text{H} = 8.50$ .

$\text{C}_9\text{H}_{16}\text{O}_4$  requires  $\text{C} = 57.45$ ;  $\text{H} = 8.51$  per cent.



The conversion of the *cis*- into the *trans*-form is partially effected by heating the *cis*-acid in a sealed tube with concentrated hydrochloric acid for 6 hours at 180°. The acids can be separated by repeated recrystallisation from water.

The conversion of the *cis*- into the *trans*-form is completely brought about by heating the *trans*-acid with acetic anhydride in a sealed tube at 150° for 4 hours. On evaporating the product and boiling with water, the *cis*-acid melting at 137° separates on cooling.

## II. Condensation of Ethyl $\alpha$ -Methylacrylate with Ethyl Sodiocyanacetate.

Ethyl  $\alpha$ -methylacrylate is best prepared by the action of diethylaniline on ethyl  $\alpha$ -bromisobutyrate. The bromo-ester (50 grams) is boiled with diethylaniline (75 grams) for 3 hours on the sand-bath. After cooling, ether is added, and the solution filtered with the aid of a pump, care being taken to thoroughly wash the diethylaniline hydrobromide with ether. The ethereal solution is then quickly shaken with dilute hydrochloric acid solution to remove excess of diethylaniline, and, after drying and distilling, fractionated. The clear, mobile liquid which passes over between 117° and 120° consists of pure ethyl  $\alpha$ -methylacrylate; it must be at once used, however, since on standing it slowly polymerises to a white, transparent substance resembling gelatine.

The largest yield of this ester was obtained by this method, but it in no case exceeded 28 per cent. of the theoretical.

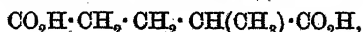
### *Condensation of Ethyl $\alpha$ -Methylacrylate with Ethyl Sodiocyanacetate.*

This condensation, in which the usual equivalent proportions of the constituents were used, was found to take place with great ease, considerable heat being evolved on adding the unsaturated ester to the alcoholic sodium compound. After heating for 1 hour on the water-bath, the product was worked up in the usual manner, and found to consist almost entirely of ethyl hydrogen salt, which, on distillation under ordinary atmospheric pressure, lost carbon dioxide and passed into *ethyl  $\gamma$ -cyano- $\alpha$ -methylbutyrate*,  $\text{CN}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{Et}$  a mobile liquid boiling at 210°. On analysis:

0.2810 gave 0.6358  $\text{CO}_2$  and 0.2076  $\text{H}_2\text{O}$ . C = 61.71; H = 8.21.

$\text{C}_8\text{H}_{13}\text{O}_2\text{N}$  requires C = 61.93; H = 8.39 per cent.

On boiling this nitrile with 50 per cent. sulphuric, it is converted, after heating for 3 hours, into  *$\alpha$ -methylglutaric acid*,



melting at  $76^{\circ}$  (Wislicenus and Limpach, *Annalen*, 1878, 192, 134).  
On analysis:

0.2701 gave 0.4872  $\text{CO}_2$  and 0.1631  $\text{H}_2\text{O}$ .  $\text{C}=49.20$ ;  $\text{H}=6.71$ .

$\text{C}_6\text{H}_{10}\text{O}_4$  requires  $\text{C}=49.31$ ;  $\text{H}=6.84$  per cent.

### III. Condensation of Ethyl $\beta$ -Methylacrylate with Ethyl Sodiocyanacetate.

Ethyl  $\beta$ -methylacrylate can be prepared in the usual way by boiling a mixture of 50 grams of ethyl  $\alpha$ -bromobutyrate and 75 grams of diethylaniline on a sand-bath for 12 hours, and since this ethyl salt shows no tendency to polymerise on standing, no special precautions are necessary in working up the product.

Ethyl  $\beta$ -methylacrylate does not condense so readily with ethyl sodiocyanacetate as the corresponding  $\alpha$ -compound, 6 hours heating on the water-bath being necessary to produce the maximum quantity of ethyl hydrogen salt, the yield of this substance, as in the former cases, being dependent on the duration of heating.

On distilling this ethyl hydrogen salt under the ordinary pressure, carbon dioxide is evolved, and it is converted into ethyl  $\gamma$ -cyano- $\beta$ -methylbutyrate,  $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , a mobile liquid boiling at  $205^{\circ}$ . On analysis:

0.2135 gave 0.4839  $\text{CO}_2$  and 0.1572  $\text{H}_2\text{O}$ .  $\text{C}=61.81$ ;  $\text{H}=8.18$ .

$\text{C}_8\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{C}=61.93$ ;  $\text{H}=8.39$  per cent.

When hydrolysed with 50 per cent. sulphuric acid, the nitrile is converted after 6 hours boiling into  $\beta$ -methylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , melting at  $86^{\circ}$  (Auwers, Köbner, and von Meyenburg, *Ber.*, 1891, 24, 2888). On analysis:

0.1956 gave 0.3526  $\text{CO}_2$  and 0.1185  $\text{H}_2\text{O}$ .  $\text{C}=49.17$ ;  $\text{H}=6.73$ .

$\text{C}_6\text{H}_{10}\text{O}_4$  requires  $\text{C}=49.31$ ;  $\text{H}=6.84$  per cent.

### IV. Condensation of Ethyl $\beta$ -Methylacrylate with Ethyl Sodiocyanacetate and subsequent Treatment with Methyl Iodide. [With H. A. NEALE.]

As explained in the general introduction (p. 932), the object of this experiment was to prepare synthetically *as-aa*-dimethylglutaric acid,  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which is of importance, since it bears upon the constitution of camphor. It was found, however, that the reaction between unsaturated esters and ethyl cyanacetate did not proceed as usually supposed, and the product obtained consisted entirely of the symmetrical *aa*-dimethylglutaric acids,



The details of the condensation between ethyl sodiocyanacetate and ethyl  $\beta$ -methylacrylate have already been given (p. 948). It was found that the length of time during which the condensation mixture must be heated to produce the maximum quantity of ethyl hydrogen salt was 6 hours; hence on treating the product after this time with excess of methyl iodide, a corresponding quantity of *ethyl  $\alpha$ -cyano- $\alpha\alpha'$ -dimethylglutarate*,  $\text{CO}_2\text{Et} \cdot \text{C}(\text{CN})(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{C}_2\text{H}_5$ , was obtained on working up the product. This ester boils at  $181-185^\circ$  under 30 mm. pressure. On analysis:

0.2214 gave 0.4839  $\text{CO}_2$  and 0.1531  $\text{H}_2\text{O}$ .  $\text{C} = 59.61$ ;  $\text{H} = 7.69$ .

$\text{C}_{12}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{C} = 59.75$ ;  $\text{H} = 7.88$  per cent.

On hydrolysis with an equal weight of potash dissolved in methyl alcohol, the ester is converted into a *potassium* salt, evidently that of the dibasic cyano-acid, which can be separated by filtration and purified by washing with methyl alcohol. On analysis:

0.5134 gave 0.3611  $\text{K}_2\text{SO}_4$ .  $\text{K} = 31.53$ .

$\text{C}_7\text{H}_9\text{O}_4\text{NK}_2$  requires  $\text{K} = 31.32$  per cent.

This salt, when its solution in water was acidified and extracted with ether, yielded a solid substance, which was not further purified but directly treated with concentrated hydrochloric acid. On boiling, a considerable quantity of carbon dioxide was evolved, which ceased after the heating had been continued for 1 hour. The solution was then extracted with ether, and the ethereal solution shaken three times with a dilute solution of sodium carbonate. On evaporating the ether, a solid remained which separated from hot water in long needles and melted at  $173^\circ$ , evidently consisting of  *$\alpha\alpha'$ -dimethylglutarimide*,  $\text{CH}_2 \begin{matrix} \text{CH}(\text{CH}_3) \cdot \text{CO} \\ \text{CH}(\text{CH}_3) \cdot \text{CO} \end{matrix} \text{NH}$  (Auwers and Thorpe, *Annalen*, 1895, 285, 315). On analysis:

0.1885 gave 16.4 c.c. nitrogen at  $17^\circ$  and 749 mm.  $\text{N} = 9.96$ .

$\text{C}_7\text{H}_{11}\text{O}_2\text{N}$  requires  $\text{N} = 9.93$  per cent.

The imide on heating for 2 hours with 50 per cent. sulphuric acid is completely hydrolysed, yielding *cis- $\alpha\alpha'$ -dimethylglutaric acid*, which separated from water in needles and melted at  $127-128^\circ$ . On analysis:

0.2237 gave 0.4295  $\text{CO}_2$  and 0.1172  $\text{H}_2\text{O}$ .  $\text{C} = 52.38$ ;  $\text{H} = 7.47$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$ ;  $\text{H} = 7.50$  per cent.

On treatment with acetyl chloride, the acid yielded an anhydride which separated from light petroleum or ethyl acetate in plates and melted at  $94-95^\circ$ . On analysis:

0.1950 gave 0.4212  $\text{CO}_2$  and 0.1223  $\text{H}_2\text{O}$ .  $\text{C} = 58.91$ ;  $\text{H} = 7.00$ .

$\text{C}_7\text{H}_{10}\text{O}_3$  requires  $\text{C} = 58.89$ ;  $\text{H} = 6.97$  per cent.

The sodium carbonate washings from the ether extract of the product of hydrolysis of the cyano-ester gave nearly pure *trans*- $\alpha,\alpha'$ -dimethylglutaric acid on acidifying and extracting with ether. The acid separated from hot water in needles and melted at  $141^{\circ}$ . On analysis:

0.2170 gave 0.4171  $\text{CO}_2$  and 0.1503  $\text{H}_2\text{O}$ . C=52.49; H=7.63.

$\text{C}_7\text{H}_{12}\text{O}_4$  requires C=52.50; H=7.50 per cent.

The acid gave no anhydride on treatment with acetyl chloride.

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### LXXXIV.—*The Persulphuric Acids*.\*

By T. MARTIN LOWRY, D.Sc., and JOHN H. WEST.

MUCH attention has been paid during the past two years in the Chemical Department of the Central Technical College to the study of the behaviour of solutions of sulphuric acid on electrolysis, as well as to the manner in which solutions of 'persulphuric' acid undergo hydrolysis. This work has been undertaken in order to elucidate the part which 'persulphuric' acid plays in the accumulator (compare Armstrong and Robertson, *Proc. R. S.*, 1891, 50, 105), and to ascertain to what extent the production of this acid must be taken into account in discussing the electric conductivity of solutions of sulphuric acid, as well as in determining the origin of the products such solutions yield when electrolysed under various conditions (compare Armstrong, Presidential Address, *Trans.*, 1895, 6, 1156).

In the course of the inquiry, it became necessary to repeat and extend Berthelot's observations on the interaction of hydrogen peroxide and sulphuric acid (*Ann. Chim. Phys.*, 1878, [v], 14, 345).

The experiments have led to results which appear to have an important bearing on the interpretation of the nature of the product formed by the interaction of sulphuric acid and potassium persulphate, which Caro (*Zeit. angew. Chem.*, 1898, 845) has shown to be possessed of special properties, and which Bamberger and von Baeyer and Villiger have recently made use of as an oxidising agent under the name of 'Caro's reagent.'

Von Baeyer and Villiger have suggested that the acid characterised by Caro is a persulphuric acid composed of hydrogen peroxide and sulphuric anhydride in the ratio  $\text{H}_2\text{O}_2:\text{SO}_3$ . The experiments described in the following pages appear to favour the conclusion that

its composition may be  $\text{H}_2\text{O}_2 : 4\text{SO}_3$ , whilst the acid, of which salts were first prepared by Marshall, is of intermediate composition,  $\text{H}_2\text{O}_2 : 2\text{SO}_3$ . The members of such a series of persulphuric acids may be provisionally distinguished as 'persulphuric,' 'perdisulphuric,' and 'pertetrasulphuric' acids.

The substance analysed by Berthelot in 1878 was the anhydride,  $\text{S}_2\text{O}_7$ , which he obtained by combining oxygen with either of the lower oxides of sulphur by means of the electric discharge. He assumed that the corresponding acid was formed on dissolving this anhydride in water, and as he found that when moderately concentrated solutions of sulphuric acid were electrolysed they acquired properties similar to those possessed by solutions of the anhydride  $\text{S}_2\text{O}_7$ , he came to the conclusion that the same acid is formed during electrolysis. The correctness of this assumption was apparently placed beyond doubt by the discovery made by Marshall in 1891 of a series of well-defined salts derived from the anhydride  $\text{S}_2\text{O}_7$ ; at all events, it has not been called in question up to the present time.

It was expressly pointed out by Berthelot in his original paper (*loc. cit.*) that persulphuric acid "se forme également, toujours à l'état dissous, lorsqu'on mélange avec précaution et en évitant toute élévation de température une solution d'eau oxygénée avec l'acide sulfurique soit concentré, soit étendu d'une quantité d'eau inférieure à 1 équivalent. Mais la combinaison n'a point lieu quand l'acide sulfurique est étendu à l'avance de 2 équivalents d'eau, ou davantage. Dans tous les cas, elle demeure partielle, c'est-à-dire qu'il subsiste une portion de l'eau oxygénée."

It will be noticed that in this passage he states that the peroxidation is confined to acids containing but a very small proportion of water. In a later paper, he discusses the formation of persulphuric acid on electrolysing solutions of sulphuric acid of various degrees of concentration, and also makes frequent reference to the production of hydrogen peroxide both during electrolysis and as a product of the decomposition of persulphuric acid; but he nowhere recognises that the proportions in which the two compounds are formed are in any way interdependent. In fact, in concluding his paper (*Ann. Chim. Phys.*, 1880, [v], 21, 193), he remarks, "Cette formation d'eau oxygénée ne paraît pas due à une réaction lente de l'eau contenue dans les liqueurs et à un équilibre résultant entre les deux composés suroxygénés, comme on aurait pu le penser d'abord. En effet, la liqueur diluée avec 20 volumes d'eau, et qui s'est conservée presque sans variation pendant neuf jours (98 mgr. réduits à 90 mgr.), n'a donné lieu à aucune formation appréciable d'eau oxygénée."

"La formation de l'eau oxygénée est donc simultanée avec la décomposition lente de l'acide persulfurique. Elle en est probable-

ment corrélatif, comme nous l'avons déjà admis plus haut pour rendre compte de sa formation par électrolyse."

Our experiments, however, lead us to conclude that in a system comprising 'persulphuric acid' and hydrogen peroxide together with sulphuric acid and water, there is a definite state of equilibrium between the two peroxidised products, and that under constant conditions the ratio of hydrogen peroxide to 'persulphuric acid' is entirely determined by the ratio of water to sulphuric acid; the ratio of hydrogen peroxide to 'persulphuric acid' is therefore ultimately the same in a mixture prepared from hydrogen peroxide and sulphuric acid as in a solution of equal strength prepared by electrolysis.

*Experimental Method.*—The method used in determining the ratio of hydrogen peroxide to 'persulphuric' acid was that used by Berthelot, and depends on the fact that whilst potassium permanganate is reduced by hydrogen peroxide, it is not affected by 'persulphuric acid,' and that the latter readily oxidises ferrous sulphate to ferric sulphate. In dilute solution at low temperatures, 'persulphuric' acid is very stable, and is not decomposed to any appreciable extent, either into sulphuric acid and oxygen, or into sulphuric acid and hydrogen peroxide; a mixture containing about 10 volumes of water to 1 volume of sulphuric acid was found to be stable at 0°, no change being perceptible in the amount of hydrogen peroxide or of 'persulphuric acid' after a week. In analysing the solutions, it is necessary that the acid should be rapidly diluted, and that no heating should take place during the dilution; if this condition is not fulfilled, the equilibrium is disturbed, and the proportion of 'persulphuric' acid is lowered accordingly. For this reason, the acid mixture was slowly delivered from a pipette on to an excess of ice, so that the temperature fell below 0° during the dilution. Special care was necessary in the case of acids containing less than one equivalent of water; these were poured directly on to a large quantity of ice without any attempt at measuring the volume of the mixture, and portions of the diluted mixture were then titrated. After diluting, the hydrogen peroxide was first estimated by running in potassium permanganate from a burette until a permanent coloration was produced. When only a small amount of hydrogen peroxide was present, it was found to be advisable to add a few drops of a solution of manganese sulphate, as otherwise the first drop of potassium permanganate produces a pink coloration, which persists for some time in the ice-cold solution, and there is a danger of overlooking the presence of hydrogen peroxide. *The interaction of hydrogen peroxide and potassium permanganate, in fact, appears to belong to the class of reactions which only take place in presence of a catalytic agent.* After determining the hydrogen peroxide, the 'persulphuric' acid was esti-

mated by adding an excess of ferrous sulphate solution, and titrating back in the usual way.

It was soon found that the ratio of 'persulphuric' acid to hydrogen peroxide was very largely influenced by minute differences in the proportions of sulphuric acid and water, and that any error in the estimation of the sulphuric acid would be reproduced five-fold in the persulphuric ratio. It was therefore necessary to take special precautions in standardising the sulphuric acid and in preparing the acid mixtures. It was, in fact, desirable that the value of the acid should be known, if possible, within 0.02 per cent., and this high degree of accuracy could only be obtained by determining the density (compare Pickering, *Trans.*, 1890, 57, 64; Marshall, *J. Soc. Chem. Ind.*, 1899, 18, 6). In all the later experiments, the acid used was drawn off by a siphon from a bottle containing about seven litres, and measured out from a repeating burette into flasks fitted with a rubber stopper and drying tube, the acid in the bottle and burette being also protected by drying apparatus. To determine the density, 10 c.c. of water were run into a dry flask and carefully mixed with about 80 grams of the acid from the repeating burette; the flask, water, and acid were weighed to 0.001 gram, and the density of the mixture was then determined at 18°, relatively to water at 18°, with the aid of a density tube about 5 c.c. in capacity. The concentration of the diluted acid could be deduced to within 0.01 per cent. from the table given by Marshall, and it was easy to calculate the concentration of the original acid from the value so found. As showing the accuracy of the method, the six values determined in the case of the acid used in the last series of experiments may be quoted, namely, 93.70, 93.81, 93.66, 93.78, 93.76, 93.76, mean value 93.75, mean error 0.04.

The mixtures to be titrated were prepared in a similar way, but 20 c.c. of hydrogen peroxide (20 vols.) were taken in place of the water, and the weighings were made to 0.01 gram only; the flasks containing the mixtures were closed by rubber stoppers each fitted with a tube drawn out to a minute capillary, in order to allow of the escape of oxygen, whilst preventing the entrance of moisture. In making the weaker mixtures, 40 c.c. of a dilute hydrogen peroxide solution was used, whilst in the case of those of higher concentration 5 c.c. of a "50 volume" hydrogen peroxide\* was taken, in order to diminish the quantity of acid required, and so as to lessen the danger due to heating during the dilution, which has already been referred to. Commercial hydrogen peroxide always contains a considerable quantity of chlorine, which is given off on mixing it with sulphuric acid; the greater part of this may be removed by adding silver

\* We were indebted for this to Mr. Tyrer, who had kindly prepared it at Dr. Armstrong's request.

sulphate, but it has been found to be necessary to leave a trace of chlorine in the solution, as the merest trace of silver suffices to render the acid mixtures so unstable that they lose the whole of their oxidising power in the course of a few hours.

Temperature does not appear to have any very marked influence on the equilibrium; a mixture which was examined to test this point gave 61.2 per cent. of persulphuric oxygen at 35° and 62.4 per cent. at 18°.

The rate at which the equilibrium is reached is very largely influenced by the concentration of the acid; in fact, it would seem that a state of equilibrium is only established when it is present in large excess; this case appears to be analogous to that of the two isodibutylenes described by Butlerow (*Annalen*, 1877, 189, 44), which undergo isomeric change, and come to a state of equilibrium only in presence of strong sulphuric acid. In the case of the more concentrated mixtures, the equilibrium is very rapidly reached, and there is little difficulty in obtaining trustworthy measurements, but in the less concentrated solutions the change takes place only slowly, and it becomes increasingly difficult to obtain concordant results.

To ascertain whether the same equilibrium could be arrived at by starting from persulphuric acid in place of hydrogen peroxide, a mixture of sulphuric acid and water was electrolysed in a divided cell, and a number of acid mixtures were prepared, using the anode acid in place of the hydrogen peroxide of the preceding experiments. A portion of the anode acid was decomposed by warming with platinum foil, and standardised by determining its density in the usual way. Owing to the additional sources of error thus introduced, these determinations are less trustworthy than those depending on the use of hydrogen peroxide, but the values obtained show a satisfactory agreement with the calculated values, as will be seen on referring to Table I, in which the mixtures prepared from electrolytic acid are marked with an asterisk.

A single experiment was also made, in which a solution of commercial 'ammonium persulphate' was used in place of hydrogen peroxide. The percentage of 'persulphuric oxygen' was found to be 90.9 when ammonium persulphate solution was used, and 90.7 in a comparison experiment with an equal volume of hydrogen peroxide.



TABLE I.—*Equilibrium between Hydrogen Peroxide and 'Persulphuric' Acid in presence of Sulphuric Acid and Water at 18°.*

Sulphuric acid per cent.	Sulphuric acid mols. per cent.	Formula of acid $\text{H}_2\text{SO}_4, n\text{H}_2\text{O}$ .	Persulphuric oxygen per cent.			$k$ .	$k_2$ .
			Obs.	Calc.	Diff.		
88.65	58.93	0.6968	96.5	98.2	-1.7		
87.0	55.2	0.8136	95.6	96.2	-0.6		
*86.86	53.71	0.8598	94.4	95.4	-1.0		
85.59	52.17	0.9169	93.1	94.2	-1.1		
*84.66	50.86	0.9858	92.7	92.4	+0.3		
84.5	50.0	1.0000	92.2	91.7	+0.5		
84.15	49.31	1.028	92.2	91.2	+1.0		
82.9	47.4	1.122	88.9	88.1	+0.8		
*82.81	46.97	1.129	87.6	88.0	-0.4	11.48	10.68
82.31	46.07	1.170	86.8	86.3	+0.5	12.37	11.51
81.7	45.0	1.219	85.3	84.3	+1.0	12.76	11.88
80.75	43.52	1.298	80.3	80.9	-0.6	11.5	10.48
80.48	43.12	1.319	80.2	79.9	+0.3	12.55	11.13
80.46	43.08	1.321	79.2	79.8	-0.6	12.0	10.89
80.08	42.47	1.355	78.4	78.3	+0.1	12.25	11.07
80.06	42.43	1.357	77.8	78.2	-0.4	11.89	10.74
79.9	42.2	1.370	77.6	77.5	+0.1	12.22	11.04
79.69	41.87	1.388	76.6	76.6	0	12.17	10.95
79.60	41.75	1.395	76.0	76.3	-0.3	12.01	10.76
79.45	41.52	1.409	75.6	75.6	0	12.19	10.95
78.96	40.82	1.450	73.2	73.5	-0.3	12.08	10.77
78.52	40.20	1.488	71.3	71.6	-0.3	12.19	10.79
78.5	39.9	1.504	70.7	70.8	-0.1	12.32	10.90
78.04	39.42	1.537	69.5	69.0	+0.5	12.72	11.24
78.01	39.39	1.539	68.8	68.9	-0.1	12.31	10.81
77.57	38.91	1.574	66.8	67.1	-0.3	12.24	10.78
77.20	38.36	1.607	65.0	65.4	-0.4	12.38	10.75
76.91	37.95	1.635	64.3	63.9	+0.4	12.88	11.20
76.91	37.95	1.635	63.9	63.9	0	12.63	10.94
76.67	37.64	1.657	62.6	62.7	-0.1	12.63	10.89
76.53	37.45	1.670	62.4	62.1	+0.3	12.92	11.20
76.44	37.36	1.677	61.3	61.7	-0.4	12.50	10.74
76.03	36.35	1.714	59.1	59.8	-0.7	12.46	10.62
75.63	36.33	1.753	57.9	57.7	+0.2	13.01	11.08
75.48	36.10	1.770	56.1	56.9	-0.8	12.56	10.58
75.18	35.74	1.798	55.5	55.4	+0.1	13.00	11.00
74.9	35.46	1.820	54.6	54.3	+0.3	13.18	11.09
74.71	35.20	1.841	52.8	53.2	-0.4	12.56	10.73
74.51	34.93	1.863	52.5	52.2	+0.3	13.33	11.14
*74.37	34.77	1.876	50.8	51.6	-0.8	12.78	10.57
73.84	34.14	1.929	49.5	49.0	+0.5	13.58	11.24
73.83	34.13	1.931	48.0	48.9	-0.9	12.85	10.50
73.18	33.41	1.993	45.6	46.1	-0.5	13.22	10.71
71.19	31.21	2.204	38.0	37.3	+0.7	14.50	11.43
71.15	31.18	2.207	37.4	37.2	+0.2	14.17	11.09
71.12	31.15	2.210	36.7	37.0	-0.3	13.87	10.80
70.48	30.50	2.279	35.1	34.5	+0.6	14.61	11.60
70.31	30.31	2.299	33.7	33.8	-0.1	14.15	10.81
69.06	29.07	2.440	28.4	29.3	-0.9	14.07	10.32

TABLE I.—*Equilibrium between Hydrogen Peroxide and 'Persulphuric' Acid in presence of Sulphuric Acid and Water at 18° (continued).*

Sulphuric acid per cent.	Sulphuric acid mols. per cent.	Formula of acid $\text{H}_2\text{SO}_4, n\text{H}_2\text{O}$ .	Persulphuric oxygen per cent.			$k_1$ .	$k_2$ .
			Obs.	Calc.	Diff.		
67.45	28.03	2.567	25.7	25.8	-0.1	15.00	10.84
66.56	26.77	2.736	21.8	21.8	0	15.82	10.96
65.64	26.00	2.847	19.4	19.6	-0.2	15.81	10.71
60.95	22.28	3.487	9.9	11.2	-1.3		
54.93	20.52	4.466	4.2	5.6	-1.4		
45.72	13.40	6.463	0.8	2.0	-1.2		

In Table I, the percentage composition of the acid is given in column 1, and the molecular percentage composition in column 2. In calculating these values, the hydrogen peroxide solution has been reckoned as water; and no attempt has been made to make any correction for the small weight of active oxygen which it contains. In column 3, the number of molecules of water per molecule of the acid is tabulated as the formula of the acid  $\text{H}_2\text{SO}_4, n\text{H}_2\text{O}$ . Column 4 gives the percentage of the total active oxygen present in the form of 'persulphuric oxygen' (that is, indifferent to potassium permanganate).

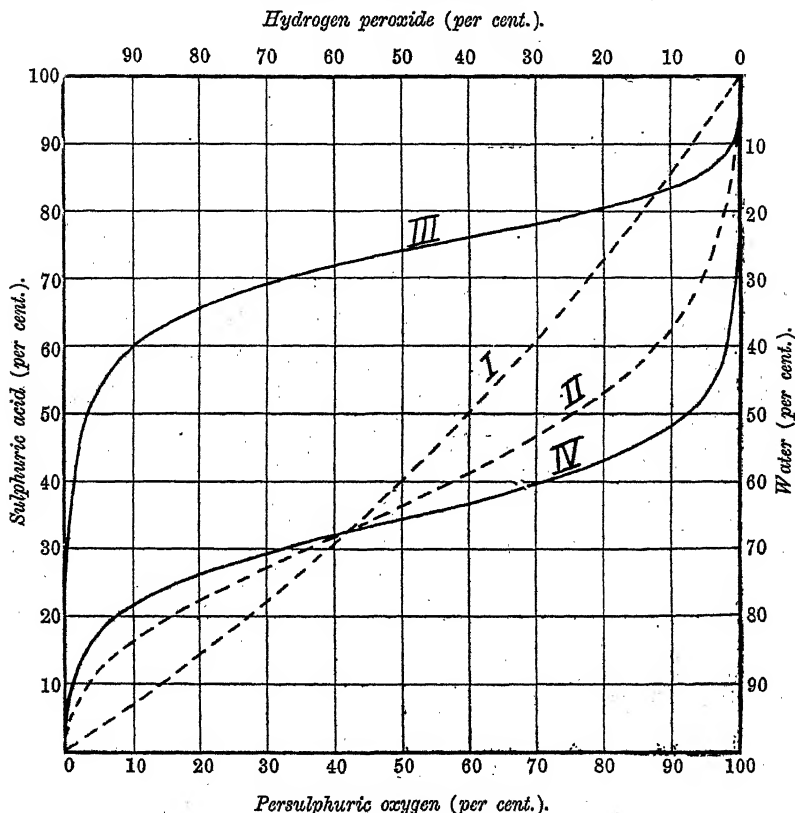
In the figure, the percentages given in column 4 are plotted as abscissæ, whilst the percentages in columns 1 and 2 are the ordinates in the curves (p. 957) marked III and IV respectively.

It will be noticed that the conversion of hydrogen peroxide into 'persulphuric' acid, and *vice versa*, takes place for the most part within very narrow limits of concentration; thus, on increasing the strength of the acid from 70 to 80 per cent., the proportion of 'persulphuric oxygen' increases from 31 to 78 per cent., an increase of 47 per cent. in the proportion of 'persulphuric' acid for an increase of only 10 per cent in the strength of the sulphuric acid. The same fact is illustrated by the proportions of 'persulphuric oxygen' corresponding to the hydrates of sulphuric acid, namely:

$\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ .....	92 per cent.
$\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ .....	46 „
$\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$ .....	17 „
$\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ .....	7 „

From this table, it appears that 85 per cent. of the change takes place between the limits  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ ; above  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$  and below  $\text{H}_2\text{SO}_4, 10\text{H}_2\text{O}$ , the change is virtually

*Curves showing the equilibrium between hydrogen peroxide and 'persulphuric acid' in presence of sulphuric acid and water.*



*Form of the Equilibrium Curve.*—The equilibrium curve for the system—sulphuric acid, water, 'persulphuric' acid, hydrogen peroxide—is extremely similar to that corresponding with the simple quartic equation

$$\frac{c_1}{c_2} = k \left( \frac{c_3}{c_4} \right)^4,$$

where  $c_1, c_2$  represent the relative molecular proportions of the 'persulphuric' acid and hydrogen peroxide, whilst  $c_3, c_4$  represent the molecular proportions of sulphuric acid and water respectively. The two curves are so similar that on the small scale of the figure it would not be possible to represent them clearly by separate lines. If, however, the values of  $k$  be calculated for each point, it is found that they steadily increase as the concentration decreases; this is clearly shown

in the table, in which the values of  $k$ , calculated on this basis, are given in column 7.

The curve can, however, be represented with a very considerable degree of accuracy by the equation

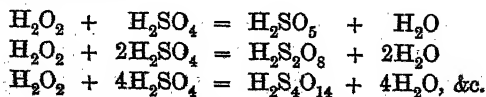
$$\frac{c_1}{c_2} = k_1 \left( \frac{c_3}{c_4} \right)^2 + k_2 \left( \frac{c_3}{c_4} \right)^4,$$

where  $k_1 = 0.63$  and  $k_2 = 10.96$ .

The percentages,  $\frac{100 c_1}{c_1 + c_2}$ , calculated from this formula, are tabulated in column 5, and the differences between the observed and calculated values are given in column 6. It could hardly be expected that a simple algebraical expression should be found which would cover the wide range of chemical change involved in diluting the sulphuric acid from 100 per cent. to 0 per cent., but fortunately in this case the greater part of the change takes place within very narrow limits of concentration, namely, between 85 and 55 per cent., and the disturbances due to the changing nature of the acid are therefore largely avoided. Between the limits of 65 per cent. and 81 per cent., within which the percentage of 'persulphuric' oxygen increases from 19 per cent. to 81 per cent., the maximum error in the 40 observations is less than 1 per cent., and the average error is 0.33 per cent.

In order to test the accuracy of the formula used, the value of  $k_1$  has been assumed to be 0.63 throughout, and the value of  $k_2$  has then been calculated for each point on the curve; the values of  $k_2$  thus obtained are given in the last column of the table, and are extremely steady throughout the series.

*Nature of the Products.*—In discussing our results, no attention has thus far been paid to the possible nature of the substances concerned in the equilibrium, and the algebraical formula arrived at is independent of any theoretical interpretation that may be given of the chemical change. It is now necessary to consider what this may be. The existence of a series of crystalline compounds containing sulphuric anhydride and water in different proportions serves to suggest that there may be a series of 'persulphuric' acids containing different proportions of sulphuric anhydride and hydrogen peroxide. The interaction of sulphuric acid and hydrogen peroxide may then be represented by equations such as



According to the law of mass-action, the equilibrium between hydrogen peroxide and the different 'persulphuric' acids would be represented by the equations

$$\begin{aligned}
 kc_2c_3 &= c_1c_4 \quad \text{or} \quad \frac{c_1}{c_2} = k\frac{c_3}{c_4} \\
 kc_2c_3^2 &= c_1c_4^2 \quad \text{or} \quad \frac{c_1}{c_2} = k\left(\frac{c_3}{c_4}\right)^2 \\
 kc_2c_3^4 &= c_1c_4^4 \quad \text{or} \quad \frac{c_1}{c_2} = k\left(\frac{c_3}{c_4}\right)^4, \quad \&c.,
 \end{aligned}$$

where  $c_1, c_2, c_3, c_4$  are the concentration of the four components of the system.

If, as Berthelot supposed, the sole product of the action were a 'perdisulphuric acid' of the formula  $\text{H}_2\text{S}_2\text{O}_8$ , the equilibrium must correspond with an equation of the second order, and would be represented by an equilibrium curve similar to II in the figure, which was plotted from the formula

$$\frac{c_1}{c_2} = 3\left(\frac{c_3}{c_4}\right)^2;$$

although this curve is similar in type to the experimental curve, it will be seen that the reversal of curvature is much less pronounced. The effect of lowering the order of the equation is seen in curve I in the figure, which was plotted from the equation

$$\frac{c_1}{c_2} = \frac{3}{2} \frac{c_3}{c_4};$$

in this curve, the reversal of curvature has entirely disappeared and the curve does not bear the slightest resemblance to the experimental curve. It is therefore evident that the experimental curve must be represented by an equation of a higher, rather than of a lower, order than the second. The formula  $\text{H}_2\text{SO}_5$  (von Baeyer and Villiger, *Ber.*, 1900, 33, 124), which actually gives curve I in the figure, must therefore be rejected.

The experimental curve, however, approximates very closely to the curve deduced from an equation of the fourth order, such as

$$\frac{c_1}{c_2} = 12.6\left(\frac{c_3}{c_4}\right)^4,$$

and assuming that the chief product of the interaction is a 'persulphuric' acid of the series  $\text{H}_2\text{O}_2, n\text{SO}_3$ , it is evident that it must be the *fourth* member, that is, its formula must be  $\text{H}_2\text{O}_2, 4\text{SO}_3$  or  $\text{H}_2\text{S}_4\text{O}_{14}$ .

The small, but steady, deviations of the experimental curve from that deduced from the simple equation of the fourth order are in the direction of the curves of lower order, and serve to indicate that along with the acid  $\text{H}_2\text{S}_4\text{O}_{14}$  there is produced a much smaller amount of some simpler acid of the series, and it appears only fair to suppose that this is the acid  $\text{H}_2\text{S}_2\text{O}_8$ , which Berthelot assumed was alone

formed. The equation for an equilibrium between  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{S}_2\text{O}_8$ , and  $\text{H}_2\text{S}_4\text{O}_{14}$  would be of the form

$$\frac{c_1}{c_2} = k_1 \left( \frac{c_3}{c_4} \right)^2 + k_2 \left( \frac{c_3}{c_4} \right)^4,$$

where  $k_1$  is the equilibrium constant for the 'perdisulphuric' and  $k_2$  that for the 'pertetrasulphuric' acid. Taking  $k_1 = 0.63$  and  $k_2 = 10.96$ , this equation gives results which agree very closely with the observed values for the equilibrium, and there can be little doubt that it represents the experimental data as closely as they can be represented by a simple algebraical equation. There is at present no method known by which the persulphuric acids may be separately estimated, but it will be of interest to record the calculated proportions of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{S}_2\text{O}_8$ , and  $\text{H}_2\text{S}_4\text{O}_{14}$  in some of the mixtures.

TABLE II.

Composition of the acid.	$\text{H}_2\text{O}_2$ .	$\text{H}_2\text{S}_2\text{O}_8$ .	$\text{H}_2\text{S}_4\text{O}_{14}$ .
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$	7.9	5.0	87.1
$\text{H}_2\text{SO}_4 + 1.50\text{H}_2\text{O}$	29.2	8.1	62.7
$\text{H}_2\text{SO}_4 + 1.99\text{H}_2\text{O}$	53.9	8.6	37.5
$\text{H}_2\text{SO}_4 + 2.57\text{H}_2\text{O}$	74.2	7.1	18.7
$\text{H}_2\text{SO}_4 + 3.49\text{H}_2\text{O}$	88.8	4.6	6.6
$\text{H}_2\text{SO}_4 + 4.47\text{H}_2\text{O}$	94.4	3.0	2.6
$\text{H}_2\text{SO}_4 + 6.46\text{H}_2\text{O}$	98.0	1.4	0.6

A qualitative test is, however, available for distinguishing the 'perdisulphates' and 'pertetrasulphates,' Caro (*Zeit. angew. Chem.*, 1898, 845) having shown that the 'perdisulphates' produce a brown precipitate in a neutral solution of aniline, but that the neutral salts of the acid formed by the interaction of 'perdisulphates' and sulphuric acid have the property of oxidising aniline to nitrosobenzene. On applying this test, it was found that a mixture of hydrogen peroxide with a large excess of sulphuric acid gave a considerable quantity of nitrosobenzene, but only a trace of the brown precipitate characteristic of the 'perdisulphates'; a mixture of hydrogen peroxide with an equal bulk only of sulphuric acid gave, however, a much more pronounced brown precipitate and only a small amount of nitrosobenzene. There can therefore be little doubt as to the presence of both 'perdisulphuric' and 'pertetrasulphuric' acids in the product, the relative proportion of 'perdisulphuric acid' being greatest in the more dilute solutions.

It is scarcely necessary to say that the conclusions we have arrived at are verified by the analytical examination of the product: but

as Caro has stated that he is engaged in completing his discovery, we have not thought it right to extend our experiments in this direction. We may mention, however, that solutions containing a very large proportion of the peroxidised acids may be obtained, not only by electrolysing solutions of sulphuric acid, but also by mixing sulphuric acid with hydrogen peroxide, and then concentrating by freezing out the hydrate  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ .

If our conclusion be accepted, it will follow that the account given by Berthelot, and, in fact, by all who have studied the acid, applies to 'pertetrasulphuric acid' rather than to 'perdisulphuric acid,' which appears under all conditions to be by far the minor product and the less stable, although its salts are more stable than those of 'pertetrasulphuric acid.' The production of 'perdisulphates' on electrolysing solutions of acid sulphates, whilst solutions of sulphuric acid yield chiefly 'pertetrasulphates,' is of interest as an indication that the electrolysis proceeds on very different lines in the two cases.

Attention may also be directed to the fact that, inasmuch as the persulphuric acids are formed by the interaction of sulphuric acid and hydrogen peroxide, it is clear that the affinity of hydrogen peroxide must be greater than that of water for sulphuric anhydride.

In conclusion, the authors desire to express their thanks to Dr. Armstrong, at whose suggestion the research was carried out, and to whom they are indebted for much valuable help during the whole course of the work.

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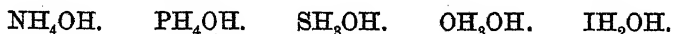
[It is proposed to extend the method here described to the study of the peroxides of other acids. H. E. A.]

### LXXXV.—*Dimethyldiacetylacetone, Tetramethylpyrone, and Orcinol Derivatives from Diacetylacetone.*

By J. N. COLLIE, F.R.S., and B. D. STEELE, B.Sc. (Melbourne),  
1851 Exhibition Scholar.

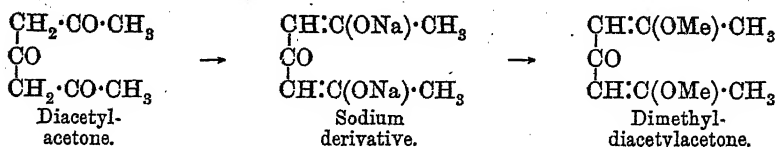
IN a paper published last year (Trans., 1899, 75, 710), one of us showed how dimethylpyrone was capable of acting as a basic substance, forming salts with various acids, and the idea was put forward that oxygen under certain conditions could replace phosphorus, nitrogen, sulphur,

or iodine in basic organic compounds owing to its quadrivalence, these compounds being supposed to be derived from the theoretical bases :

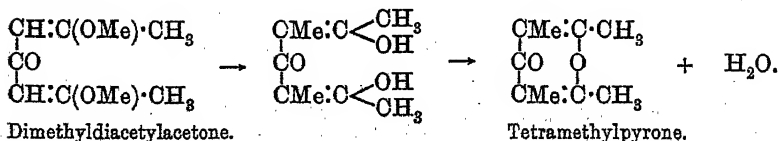


The present work was undertaken in order to see whether the property of forming these salts was peculiar to dimethylpyrone alone, or was shared by other pyrone compounds.

Diacetylacetone, when allowed to react with sodium ethoxide, at once yields a disodium derivative. This, when treated with methyl iodide, should yield dimethyldiacetylacetone, which should give tetramethylpyrone when boiled with acids or when heated :



The change undergone by dimethyldiacetylacetone when boiled with acids is due to molecular rearrangement and subsequent elimination of water :



This tetramethylpyrone should have properties closely resembling those of dimethylpyrone, and we expected that, owing to the greater number of methyl groups, it might form salts with even greater ease than the latter. We also hoped that the yield would be nearly quantitative. In both cases we were disappointed; the yield is by no means good, several other compounds being produced at the same time, and the basic properties of tetramethylpyrone do not seem to be so well marked as those of dimethylpyrone. The platinichloride separates at once when a moderately strong solution of platinic chloride is added to a solution of the base in hydrochloric acid, but with other acids crystallisable salts are not easily formed.

Although the original object of the investigation has not been attained to the extent that we had hoped, yet the side issues that have opened out are of considerable interest, and the other compounds produced by the reaction show how easily, by means of another kind of condensation, benzene and naphthalene derivatives can be formed.

The substances separated from the product after the action of methyl iodide on disodium diacetylacetone are the following :

Dimethyldiacetylacetone,  $\text{C}_8\text{H}_{14}\text{O}_5$ , m. p. 86—87°.



- (2) Tetramethylpyrone,  $C_9H_{12}O_2$ , m. p.  $92^\circ$ .
- (3) Hydrate of tetramethylpyrone,  $C_9H_{14}O_3$ , m. p.  $63-64^\circ$ .
- (4) (?) Trimethyldihydroxybenzene,  $C_9H_{12}O_2$ , m. p.  $150^\circ$ .
- (5) (?) Trimethyldihydroxybenzene,  $C_9H_{12}O_2$ , m. p.  $105-106^\circ$ .
- (6) Trimethylpyrone,  $C_8H_{10}O_2$ , m. p.  $78^\circ$ .
- (7) Dimethylacetodihydroxynaphthalene,  $C_{14}H_{14}O_3$ , m. p.  $183-184^\circ$ .

The reaction is one, therefore, of some complexity, but is an excellent example of how simple condensation of molecules containing the complex  $\cdot CH_2 \cdot CO \cdot$  or its enolic form  $\cdot CH : C(OH) \cdot$  may be brought about in an alkaline solution.

#### EXPERIMENTAL.

When diacetylacetone is dissolved in absolute alcohol and a molecular equivalent of sodium ethoxide added, an insoluble salt is not obtained, but with more sodium ethoxide, a white, crystalline sodium compound separates. Fifty grams of diacetylacetone were dissolved in absolute alcohol, and sodium ethoxide made from 20 grams of sodium (calculated amount for  $2Na = 16.2$  grams), dissolved also in absolute alcohol, was added. The sodium salt that crystallised out was washed and dried; when pure, it has a blue fluorescence. On analysis:

Found,  $Na = 22.6$  and  $22.8$ .  $C_7H_{10}O_4Na_2$  requires  $Na = 22.5$  per cent.

This sodium salt was suspended in alcohol and boiled with 105 grams of methyl iodide (an excess of 5 grams) until the contents of the flask were neutral. The spirit was removed by distillation, and the residue treated with water and extracted with chloroform. After the chloroform had been distilled off in a water-bath, the residue was fractionated under 15—20 mm. pressure. Several fractions were obtained; the bulk of the distillate (25—30 grams), however, was collected between  $125^\circ$  and  $150^\circ$ . This portion, on standing, became semi-solid. It was transferred to a porous plate, and the resulting crystals recrystallised from water. When pure, it melted at  $86-87^\circ$ , and boiled with much decomposition at  $230-240^\circ$  under ordinary atmospheric pressure. On analysis, the substance proved to be dimethyldiacetylacetone:

Found  $C = 63.1$ ;  $H = 8.2$  per cent.

$C_9H_{14}O_3$  requires  $C = 63.5$ ;  $H = 8.2$  per cent.

The results of several other experiments were as follows: 10 grams of diacetylacetone gave 6 grams boiling at  $120-150^\circ$  under reduced pressure; 30 grams gave 17 grams, and another 30 grams yielded 19 grams. During the reaction between methyl iodide and disodium diacetylacetone, it is absolutely necessary that the alcohol and other substances should be perfectly dry; if this is not the case, considerable quantities of a yellow resin, mainly dimethylacetodihydroxynaphthalene (Trans., 1893, 63, 334), are formed.

Dimethyldiacetylacetone is a white, crystalline substance melting at 86—87°. It can be recrystallised from water in groups of needles. With ferric chloride, it gives a purple coloration. Unlike diacetylacetone, it only gives a slight precipitate when boiled with barium hydroxide. When boiled, however, with caustic soda, decomposition occurs. Five grams of dimethyldiacetylacetone were boiled with rather more than 2 mols. of *N*-sodium hydroxide. From the residue were separated (1) a small amount of methyl alcohol and some sodium acetate, (2) about 0.5 gram of methyl ethyl ketone (b. p. 80—81°), (3) 1.5 grams of a substance crystallising in needles (m. p. 92°), which was readily volatile with steam, yielded a platinichloride, and proved to be tetramethylpyrone. The crystals were analysed:

Found C = 70.7; H = 7.9.

$C_9H_{12}O_2$  requires C = 71.0; H = 7.9 per cent.

From the action of sodium hydroxide on dimethyldiacetylacetone, it is evident that part of the latter exists in the form of a methoxy-compound, otherwise it is very unlikely that any methyl alcohol would be produced; a considerable portion, however, undergoes molecular change, water is eliminated, and tetramethylpyrone is formed. Dimethyldiacetylacetone, when boiled with hydrochloric acid, soon loses its power of giving a purple colour with ferric chloride. Tetramethylpyrone remains in the solution, and as this substance is volatile with steam, it is best to effect the change by digesting the diacetylacetone and acid in a flask connected with a reflux condenser. When the reaction is complete, the acid is nearly neutralised with soda and the liquid extracted with chloroform. The chloroform is removed by distillation, and the residue mixed with a little water and allowed to crystallise. A hydrate of tetramethylpyrone separates. This was recrystallised several times from water, and was then obtained in the form of colourless needles melting at 63—64°. On analysis:

Found C = 63.0; H = 8.3; also C = 63.3; H = 8.4.

$C_9H_{12}O_2 \cdot H_2O$  requires C = 63.5; H = 8.2 per cent.

This hydrate easily loses water if heated or left over sulphuric acid in a vacuum; it then melts at 92° and boils at 245°. On analysis:

Found C = 71.0; H = 8.0.

$C_9H_{12}O_2$  requires C = 71.0; H = 7.9 per cent.

The dehydration can also be effected by recrystallising the hydrate from light petroleum, when colourless, transparent plates melting at 92° are obtained. Also if the fused hydrate is kept for some time, and then allowed to cool and crystallise, the melting point is found to be 92°. These crystals are changed back again to the hydrate (m. p. 64°) when put into water. Another curious

change in melting point is shown by the tetramethylpyrone (m. p.  $92^{\circ}$ ). If it is kept melted for a short time after crystallising, its melting point is found to be about  $77^{\circ}$ . This, however, may be due to partial decomposition.

Tetramethylpyrone easily dissolves in hydrochloric acid, and if platinic chloride is added to this solution a yellow platinichloride soon crystallises out. It was found best to recrystallise this salt by dissolving it in warm water and then allowing the aqueous solution to evaporate. Should the solution be boiled, decomposition occurs and a resinous material containing platinum separates. After two recrystallisations, it was considered to be pure, and was analysed:

Found C = 28.5; H = 4.0; Pt = 25.8 and 26.0.

$(C_9H_{12}O_2)_2 \cdot H_2PtCl_6 \cdot 2H_2O$  requires C = 28.8; H = 4.0; Pt = 26.0 per cent.

It was not found possible to estimate the water of crystallisation, for when heated, or even left in a vacuum desiccator, the double salt loses tetramethylpyrone as well as the water. That it did contain water of crystallisation was proved by heating some in a tube when water was driven off. This was found to be the case with tetramethylpyrone hydrate as well; some of this compound (m. p.  $64^{\circ}$ ), left in a vacuum over sulphuric acid for 24 hours, lost 13.6 per cent. of its weight, the calculated loss of weight being 10.6 per cent.

Tetramethylpyrone dissolves readily in water, and then the hydrate crystallises out. It differs in some respects from dimethylpyrone; for instance, it does not give a precipitate with barium hydroxide, even after prolonged boiling, also it does not seem to form salts with mineral acids nearly so readily as dimethylpyrone. Potassium permanganate has no action on it in the cold, and it does not reduce silver nitrate solution. When warmed with strong sulphuric acid, it turns faintly yellow, and the aqueous solution gives a pink coloration with caustic soda. Ferric chloride gives no coloration.

Tetramethylpyrone hydrochloride is formed in long, needle-shaped crystals when a solution of the base is mixed with hydrochloric acid and allowed to evaporate. It is a very unstable salt, being instantly decomposed by water into tetramethylpyrone hydrate and hydrochloric acid. Also when left for a week in contact with air, nearly all the hydrogen chloride has evaporated away. Some was dried on a porous plate and analysed.

Found Cl = 9.0.  $(C_9H_{12}O_2)_2 \cdot HCl \cdot 2H_2O$  requires Cl = 9.4 per cent.

The substance, when heated, yields water, hydrogen chloride, and tetramethylpyrone.

Tetramethylpyrone hydriodide also can be obtained in the form of

needle-shaped crystals by the same method, but another crystalline compound is formed at the same time by the action of free iodine on the salt. This free iodine is produced by the decomposition of the excess of hydriodic acid.

An attempt to prepare the oxalate was made, but without success. The calculated quantity of oxalic acid was added to a solution of the base, and the whole allowed to slowly evaporate in a desiccator, but only tetramethylpyrone hydrate crystallised out.

The same result was obtained with a solution of the sulphate. When nitric or hydrobromic acids are added to the solid tetramethylpyrone, heat is evolved, but even after the solutions thus obtained had been left for several days in a vacuum over caustic soda no crystalline substance separated, the remaining salts consisting of syrupy solutions, which, when tested, were found to contain considerable amounts of the respective acids.

The yield of dimethyldiacetylacetone from disodium diacetylacetone and methyl iodide was never greater than 50 per cent. of the theoretical; the residues, after extraction with chloroform, were therefore examined. When shaken out with ether, small quantities of a substance melting at  $150^{\circ}$  were obtained; then on extraction with benzene another compound was separated, which, after recrystallisation from light petroleum, melted at  $78^{\circ}$ . The aqueous residue, chiefly consisting of sodium iodide, was evaporated to dryness and distilled in a vacuum, a crystalline sublimate was obtained, which, after recrystallisation, melted at  $150^{\circ}$ , and was identical with the compound extracted in small quantities from the aqueous solution by means of ether.

The compound melting at  $150^{\circ}$  gave, with ferric chloride, a green coloration rapidly turning to a grey precipitate, whilst that melting at  $78^{\circ}$  gave no reaction with ferric chloride, but formed a crystalline platinichloride with platinic chloride solution.

*Compound melting at  $78^{\circ}$ . Trimethylpyrone,  $C_8H_{10}O_2$ .*

Unfortunately, only a very small quantity of this substance was obtained. It is very soluble in water, but eventually was found to crystallise in well-defined prisms from light petroleum. On analysis :

Found  $C = 69.3$  ;  $H = 7.5$ .

$C_8H_{10}O_2$  requires  $C = 69.5$  ;  $H = 7.3$  per cent.

That it possesses basic properties is proved by the existence of the platinichloride, which was also analysed.

Found  $C = 26.6$  ;  $H = 3.6$  ;  $Pt = 27.0$ .

$(C_8H_{10}O_2)_2 \cdot H_2PtCl_6 \cdot 2H_2O$  requires  $C = 26.6$  ;  $H = 3.6$  ;  $Pt = 27.0$  per cent.

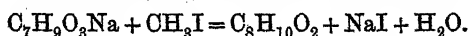
As such a very small quantity of this substance had been obtained by extracting the aqueous residues with benzene, it was thought that possibly it might be found in the first portion of the distillate, before dimethyldiacetylacetone had distilled over. The fraction boiling between  $115^{\circ}$  and  $120^{\circ}$  under 15—20 mm. pressure was examined, and from it a small quantity of a platinichloride was produced, which, after recrystallisation, was analysed.

Found C = 27.4; H = 3.7; Pt = 26.7.

$(C_8H_{10}O_2)_2, H_2PtCl_6, 2H_2O$  requires C = 26.6; H = 3.6; Pt = 27.0 per cent.

The quantity obtained, however, was very small, and as the analysis showed that the platinum salt was contaminated with one of a higher molecular weight, presumably that of tetramethylpyrone, the investigation was not carried further.

This trimethylpyrone had evidently been produced by the action of methyl iodide on a monosodium derivative of diacetylacetone,



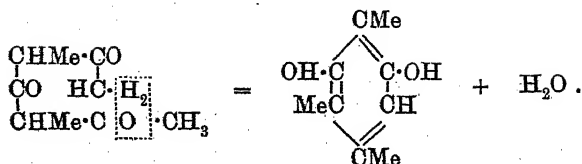
*Compound melting at  $150^{\circ}$ . Trimethyldihydroxybenzene (?)*

This substance was purified by several recrystallisations from water, and after the melting point had risen to  $150^{\circ}$  several further recrystallisations did not change it. On analysis:

Found C = 70.8 and 71.0 H = 8.1 and 8.0.

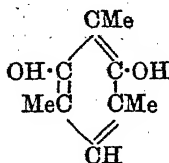
$(CH_3)_3C_6H(OH)_2$  requires C = 71.0; H = 7.9 per cent.

When heated, it sublimes. It is neutral to litmus paper. With ferric chloride, it gives first a green colour, then a grey precipitate. In all these properties, and also in its melting point, it exactly resembles mesorcinol, but its acetyl derivative melts at  $73^{\circ}$ , whilst diacetyl-mesorcinol melts at  $63^{\circ}$ ; the boiling point of this substance (m. p.  $150^{\circ}$ ) seems to differ from that of mesorcinol, being somewhere near  $290^{\circ}$ , but with such small quantities as could be used the boiling point could not be determined with accuracy. Mesorcinol is said to boil about  $275^{\circ}$ . When heated with caustic soda, alcohol, and chloroform, it at once gives a deep red colour, and the aqueous solution has a green fluorescence. Left in contact with ammonia vapour, it becomes a deep red colour. When oxidised with ferric chloride and then distilled, a yellow quinone in the distillate gives the reaction first noticed by Fittig, namely, a purple colour with alkalis which is discharged by acids. Mesorcinol is said to give this last reaction as well, but in spite of all these resemblances to mesorcinol, it is not evident how such a substance could be produced from dimethyldiacetylacetone by condensation;

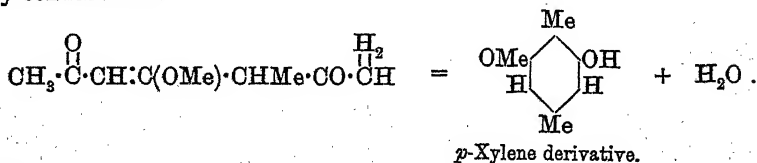


Dimethyldiacetylacetone. 1:2:4-Trimethyl-3:5-dihydroxybenzene.

Mesorcinol is undoubtedly a mesitylene derivative, and therefore can only have the following formula:



Still, it is said to give a quinone on oxidation with ferric chloride, although all the ortho- and para-positions are already occupied by methyl groups. Moreover, to make it more confusing, Kraus (*Monatsh.*, 1891, 12, 203) has prepared a trimethylresorcinol, which he says is the 1:2:4-trimethyl-3:5-dihydroxybenzene, and melts at 156°. The substance obtained from the residues in the preparation of tetramethylpyrone undoubtedly melts at 150°, and in every respect, with the exception of the boiling point and the melting point of the acetate, resembles mesorcinol. An attempt was therefore made to prepare mesitylene from it by heating with zinc dust, and 1.5 grams thus treated gave about 1 c.c. of a hydrocarbon which was found to boil at 137—138°. As mesitylene boils at 163°, it could not be that substance. *m*- and *p*-Xylene, however, boil at about 137°. An attempt was made to prepare from this small quantity of hydrocarbon the trinitro-*m*-xylene melting at 176°, but without success, and it is doubtful which of these two hydrocarbons it was. It is not probable that either *m*- or *p*-xylene could be obtained from a mesitylene derivative, but from a dimethylmethoxyhydroxybenzene such substances are to be expected. The formation of such a substance from diacetylacetone could either take place by the production of orcinol first (*Trans.*, 1893, 63, 122), and subsequent methylation, or directly from dimethyldiacetylacetone by condensation:



Under no conditions, however, could the methyl groups be found in the

meta-position as they are supposed to be in mesorcinol. It is also difficult to understand how isoxyloquinone can be produced from mesorcinol by boiling with ferric chloride, although Knecht states such to be the case (*Annalen*, 1882, 215, 100). The above *p*-xylene derivative, however, would at once give such a compound. The presence of a methoxy-group in the compound melting at  $150^{\circ}$  is, however, doubtful, for it can be boiled with fuming hydriodic acid without any change being effected, the original compound being recovered.

*Compound melting at  $105^{\circ}$ . Trimethyldihydroxybenzene (?)*

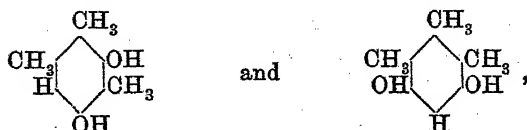
During one experiment in the preparation of dimethyldiacetylacetone, an attempt was made to prepare tetramethylpyrone directly from the product of the action of methyl iodide on disodium diacetylacetone. After the spirit had been evaporated off, the residue, consisting of sodium iodide and presumably dimethyldiacetylacetone, was treated with hydrochloric acid and boiled. Instead of obtaining tetramethylpyrone hydrate, an oil separated, from which a crystalline substance melting at  $105$ – $106^{\circ}$  was obtained. This experiment was repeated with the same result. On analysis :

Found C = 71.1. C = 8.15.

$C_9H_{12}O_2$  requires C = 71.0 ; H = 7.9 per cent.

Although this substance is identical in its composition with tetramethylpyrone,  $C_9H_{12}O_2$ , yet in properties it is entirely different from it. That it is a benzene derivative is evident from various reactions. With ferric chloride, it gives a grey precipitate ; with caustic soda, a pink solution after warming ; with caustic soda, alcohol, and chloroform, a red solution, which on diluting shows a brilliant green fluorescence. Strong sulphuric acid gives first a green coloration, then yellow ; on adding water, a precipitate forms, which dissolves in soda to a bright red, and the solution shows a green fluorescence. In all these tests, it resembles the substance melting at  $150^{\circ}$ . An attempt was made to convert it into that compound by boiling with hydrochloric acid, but without success, the original substance melting at  $105^{\circ}$  being recovered. A small amount was boiled with acetyl chloride and a drop of sulphuric acid, and an acetyl compound melting at  $70^{\circ}$  was obtained. The quantity of substance, however, was so small that no further experiments could be tried with it. Hydriodic acid has no action on it when the two are boiled together, and the original substance (m. p.  $105$ – $106^{\circ}$ ) was recovered. As this compound resembles the compound melting at  $150^{\circ}$  so closely in all its reactions, the two must be similarly constituted, and both are derivatives of orcinol. From diacetylacetone, sodium ethoxide, and

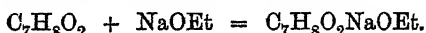
methyl iodide, only two trimethyldihydroxybenzenes are likely to be formed:



but whether the two compounds melting at  $150^\circ$  and  $105^\circ$  respectively are these substances, it is at present impossible to say.

#### *Ethyldiacetylacetone (?)*

Dimethylpyrone, when dissolved in absolutely dry alcohol, reacts with sodium ethoxide to form an additive product, which is soluble in hot alcohol, but crystallises out again on cooling.



If the alcohol is not dry, then the disodium derivative of diacetylacetone is produced, which is almost insoluble in boiling alcohol. The sodium salt was analysed:

Found Na = 12.5.  $\text{C}_7\text{H}_8\text{O}_2\text{NaOEt}$  requires Na = 12.0 per cent.

When this salt is dissolved in water and dilute acid added, a white, crystalline substance separates, which gives a blue colour with ferric chloride. It was recrystallised from light petroleum, and melts at  $57-58^\circ$ . On analysis:

Found C = 63.5. H = 8.3.

$\text{C}_9\text{H}_{14}\text{O}_3$  requires C = 63.5 and H = 8.2 per cent.

On warming with dilute hydrochloric acid, this substance, instead of being converted into dimethylethylpyrone, loses alcohol and gives dimethylpyrone. The dimethylpyrone was extracted by chloroform, converted into the platinichloride, and analysed. Three separate fractions of this salt gave the following numbers:

Found Pt = 29.6, 29.9 and 29.8.

$(\text{C}_7\text{H}_8\text{O}_2)_2, \text{H}_2\text{PtCl}_6$  requires Pt = 29.4 per cent.

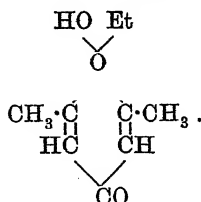
The melting point of the dimethylpyrone was also determined, and found to be  $132^\circ$ .

The substance  $\text{C}_7\text{H}_8\text{O}_2\text{EtOH}$ , when heated, decomposes almost entirely into dimethylpyrone and alcohol. The dimethylpyrone was recognised by its boiling point,  $249^\circ$ , and melting point,  $132^\circ$ . An analysis of its platinichloride was also made. Found Pt = 29.8 per cent.

From the curious behaviour of this substance, and the ease with



which it decomposes, it seems possible that it may have its molecular structure expressed by the following graphic formula:



That it is not dimethylpyrone with alcohol of crystallisation is proved by the blue colour it produces with ferric chloride, and by the fact that it may be recrystallised from water or light petroleum; also it cannot be ethoxydiacetylacetone, as this, like acetylacetone and diacetylacetone, would probably give a blood red colour with ferric chloride.

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SOCIETY OF GREAT BRITAIN.

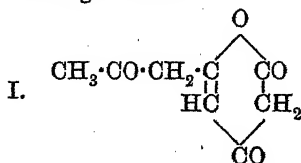
### LXXXVI.—*Dehydracetic Acid.*

By J. N. COLLIE, F.R.S.

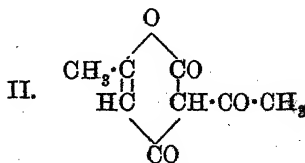
SOME years ago, the author, in conjunction with Mr. Le Sueur (Trans., 1894, 65, 254), published a paper on the salts of dehydracetic acid, in which an attempt was made to answer the question whether dehydracetic acid,  $\text{C}_8\text{H}_8\text{O}_4$ , was a lactone or a true acid. If the acid were a lactone, then the salts would have the general formula  $\text{C}_8\text{H}_7\text{O}_5\text{M}'$ . This was found to be true of all the salts until they were heated to about  $120^\circ$ , then they lost water, and their composition could be expressed by the formula  $\text{C}_8\text{H}_7\text{O}_4\text{M}'$ . Whether this water, driven off at  $120^\circ$ , was water of crystallisation or water of constitution was impossible to say. Although dehydracetic acid turns blue litmus paper red, and liberates carbon dioxide from sodium carbonate, yet it certainly cannot contain a carboxyl group, for its low dissociation constant at once negatives such an idea. Ostwald found its dissociation constant to be 0.0004, and Prof. J. Walker, who has kindly redetermined it from a pure specimen of dehydracetic acid that had been recrystallised from several different solvents, found it to be 0.0001.

There is therefore little doubt that dehydracetic acid is not a true

acid, but a lactone, and that its constitution is represented by one of the following formulæ:

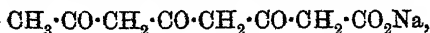


Lactone of tetracetic acid.

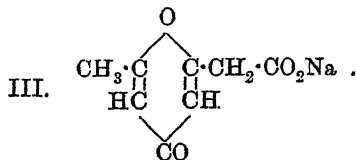


Feist's lactone formula.

Taking formula I as representing dehydracetic acid, then it is possible that the sodium salt,  $C_8H_9O_5Na$ , may be represented as follows:

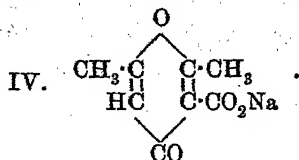


and by drying at  $120^\circ$  this salt would lose water and leave a derivative of dimethylpyrone,



At first sight this explanation seemed probable, for the amount of water present in almost every salt analysed was just sufficient to account for the difference between a salt of tetracetic acid,  $C_8H_{10}O_5$ , and of dehydracetic acid,  $C_8H_8O_4$ .

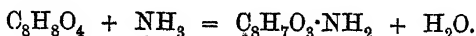
By using formula II, and representing the elimination of water in the same manner, the sodium salt would be



The question of the correct graphic formula for dehydracetic acid is one of some interest, not only because of the great variety of compounds that can easily be obtained from it—such as diacetylacetone or pyridine, isoquinoline, benzene, or naphthalene compounds, &c.—but also on account of the peculiar nature of dehydracetic acid and its salts. To take one instance, the methyl ether, Prof. W. H. Perkin (*Trans.*, 1887, 51, 497) says: "I have found it (the methyl ether) to possess most remarkable properties . . . it has a decidedly acid reaction to litmus paper . . . with potash it is instantly saponified, even in the cold. If . . . mixed with an ethereal solution of sodic acetate (1 mol.), a pink sodium compound is precipitated."

The ordinary sodium and potassium salts of dehydracetic acid'  $C_8H_9O_5M$ , are colourless, but when dried ( $C_8H_7O_4M$ ) are bright lemon-yellow; on redissolving in water, they again become colourless. The copper salt is slightly volatile when heated. With excess of caustic alkali, no xantho-salts are produced; in this respect dehydracetic acid differs from chelidonic and meconic acids.

When dehydracetic acid is dissolved in ammonia and the solution evaporated, all the ammonia is easily driven off, and the acid remains unchanged. If, however, dehydracetic acid is treated with the strongest solution of ammonia, combination occurs and an amino-compound is formed:



This amino-compound, when warmed with caustic soda, yields up all its nitrogen as ammonia, and sodium dehydracetate remains. But if dehydracetic acid is heated under pressure at  $130^\circ$  with strong ammonia solution, lutidone is formed, which is not decomposed when boiled with caustic soda.

In order to find out whether the anhydrous salts are to be represented by formula III or IV, several experiments have been tried.

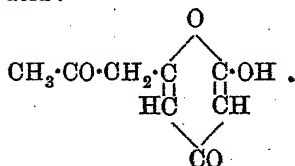
When the carefully dried yellow sodium salt is added to pure sulphuric acid, it dissolves; if the mixture is then poured into powdered ice, dehydracetic acid at once separates. Dry hydrogen chloride reacts in a similar manner, and pure dehydracetic acid can be distilled off from the sodium chloride, or can be dissolved out by means of absolute alcohol. The perfectly dry lead salt, when decomposed by dry hydrogen sulphide, gives a quantitative yield of dehydracetic acid, and the dried silver salt, when allowed to react with dry hydrogen chloride, gives only dehydracetic acid.

These results not only show that formulæ III and IV cannot possibly express the molecular construction of the salts of dehydracetic acid, but also point to the conclusion that the dehydrated salts are certainly not derivatives of an acid,  $C_8H_{10}O_5$ . Finally, if pure zinc oxide (ignited) is boiled for several hours with excess of dehydracetic acid dissolved in absolute alcohol, it is almost entirely converted into zinc dehydracetate. In one experiment, the residual zinc salt contained  $Zn = 21.7$  per cent., and in another  $Zn = 20.6$  per cent.  $(C_8H_7O_4)_2Zn$  requires  $Zn = 16.2$  per cent.

Dehydracetic acid therefore must be a compound having a molecular structure which is best represented by formula I or II, or by tautomeric modifications of I or II.

If I be accepted as the graphic formula for dehydracetic acid, then an explanation of these various compounds and properties of the acid

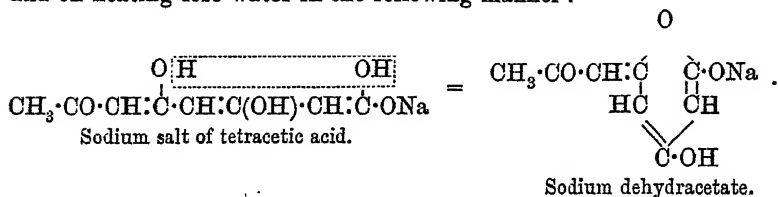
can be offered. The following tautomeric modification of I best represents dehydracetic acid :



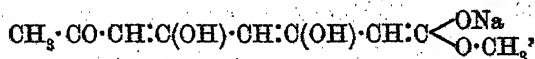
The hydrated salts of dehydracetic acid are represented by the formula :



and on heating lose water in the following manner :

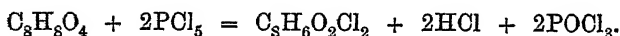


Moreover, such a compound might be expected to be coloured, as it possesses three alternate double linkings, which is a colour grouping. Also, should the sodium be replaced by a methyl group, the substance might still possess as much acidity as dehydracetic acid, whilst by the addition of sodium hydroxide and the opening up of the ring, a coloured salt could be formed,

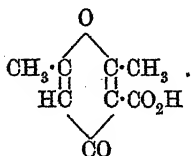


which in presence of water would instantly be hydrolysed. The volatility of the copper salt, the non-existence of xantho-salts, and the action of ammonia on dehydracetic acid also find an easy explanation by means of this formula, although formula II would do equally as well for the purpose.

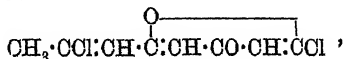
There is, however, one reaction of dehydracetic acid which can only be explained by formula I, namely, that with phosphorus pentachloride. Two hydroxyl groups are replaced, and a dichloride formed.



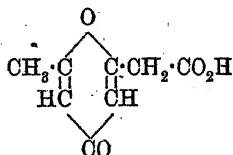
A compound represented by formula II could not possibly yield such a derivative. Moreover, Feist (*Annalen*, 1890, 257, 253) has shown that when this dichloride is heated with sulphuric acid, a true carboxylic acid isomer with dehydracetic acid, is produced. He gives it the following formula :



When heated, this acid at once loses carbon dioxide, and dimethylpyrone remains. If formula I represents dehydracetic acid, then the dichloride would be :



and by hydrolysis and loss of hydrogen chloride, an acid,



would remain, which, on heating, should give dimethylpyrone and carbon dioxide, and also possess properties similar to those of acetic acid.

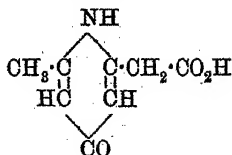
Some of the dichloride of dehydracetic acid was therefore prepared, and from it the isomeric acid,  $\text{C}_5\text{H}_8\text{O}_4$ . The silver salt of this acid crystallises in plates very similar in appearance to silver acetate; moreover, when boiled with baryta water, acetone and acetic acid are at once produced.

The action of ammonia on the acid was investigated. It was heated with excess of ammonia on a water-bath. An acid melting at  $258^\circ$  (corr.) was obtained, which, in properties, resembled in every respect the lutidonecarboxylic acid obtained from ethyl  $\beta$ -aminocrotonate by heating.

Its silver salt was analysed :

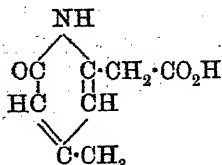
Found  $\text{Ag} = 39.6$ .  $\text{C}_5\text{H}_8\text{O}_4\text{NAg}$  requires  $\text{Ag} = 39.4$  per cent.

This acid probably has the formula

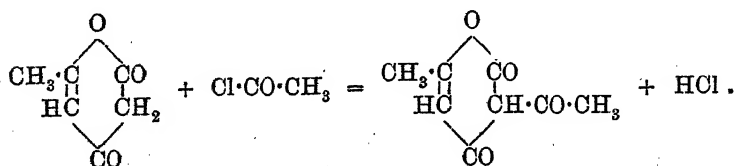


for the following reasons. When melted, it decomposes quantitatively into lutidone and carbon dioxide. Its salts are easily decomposed; for instance, a solution of the barium salt, when warmed and shaken

with carbon dioxide, yields barium carbonate and lutidone. The above reactions are not characteristic of an ordinary acid of the pyridine series, but are more in keeping with those of a substituted acetic acid; they also resemble in a marked manner those of an isomeric hydroxy-lutidinic acid (Trans., 1897, 71, 311), whose constitution is almost certainly represented by the following expression:



A further set of experiments was tried with the object of producing dehydracetic acid from triacetic lactone. If formula II represents the molecular structure of dehydracetic acid, it should not be difficult to reproduce dehydracetic acid from triacetic lactone by means of acetyl chloride.



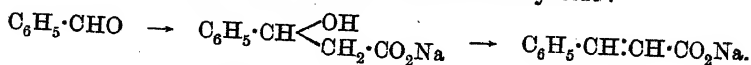
Triacetic lactone was heated with both acetyl chloride and acetic anhydride. With acetyl chloride, no change occurred, and by prolonged boiling with acetic anhydride only traces of dehydracetic acid were produced. Silver triacetate also, when dried and then added carefully to acetyl chloride, gave only triacetic lactone, after evaporating off the excess of the reagent and extracting the silver chloride with water.

Under certain conditions, however, dehydracetic acid can be made from triacetic lactone, namely, when it is boiled for some time with sulphuric acid and excess of acetic anhydride. The substance thus obtained possessed all the properties of dehydracetic acid. It melted at 108—109°. After boiling with hydrochloric acid, the concentrated solution gave a precipitate of dimethylpyrone platinichloride. This was analysed:

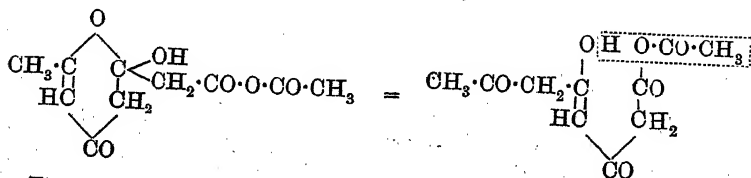
Found Pt = 29.7.  $(\text{C}_7\text{H}_5\text{O}_2)_2, \text{H}_2\text{PtCl}_6$  requires Pt = 29.6 per cen

The dimethylpyrone was also converted into the yellow barium salt, and this substance, when dissolved in dilute hydrochloric acid, gave triacetic lactone, which was recognised by the blood-red colour it gave with ferric chloride.

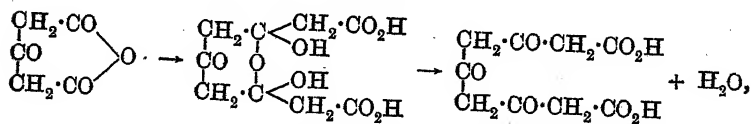
The conversion of triacetic lactone into dehydracetic acid seems to be very similar to that of benzaldehyde into sodium cinnamate by means of sodium acetate in presence of acetic anhydride:



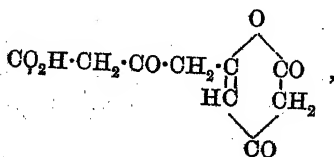
The sulphuric acid enables the sodium acetate or acetic anhydride to form an additive product with triacetic lactone, and by the elimination of acetic acid, dehydracetic acid is formed:



The connection between acetonedicarboxylic acid and dehydracetic acid (von Pechmann, *Ber.*, 1891, 24, 3600) can be explained in a similar manner. By the action of acetic anhydride, acetonedicarboxylic anhydride is first formed; this reacts with the acetic anhydride to form a dicarboxylic acid, which, when heated, loses carbon dioxide and water, and dehydracetic acid remains:



the last acid, diacetylacetonedicarboxylic acid, being at once converted into the lactone,



which decomposes, when heated, into dehydracetic acid and carbon dioxide.

RESEARCH LABORATORY OF THE PHARMACEUTICAL  
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### LXXXVII.—*Decomposition of Hydroxyamidosulphates by Copper Sulphate.*

By EDWARD DIVERS and TAMEASA HAGA.

WHEN copper sulphate is added to a solution of a hydroxyamidosulphate and the mixture heated, the acid of the salt is quickly decomposed into water, sulphur dioxide, sulphuric acid, amidosulphuric acid, and nitrous oxide, with possibly a little nitrogen. By itself, a heated solution of an alkali hydroxyamidosulphate is in a state of very unstable equilibrium, generally hydrolysing into a solution of hydrogen hydroxylamine sulphate, and always doing so in presence of a trace of acid, whilst in presence of even a trace of alkali it slowly passes into sulphite and hyponitrite (Trans., 1889, 55, 766). In the cold, with alkali and copper salt, the hydroxyamidosulphate becomes oxidised at once to sulphite, sulphate, nitrous oxide, and water, with reduction of the cupric hydroxide (*op. cit.*, 770), and when heated with cupric chloride it reduces the latter to cuprous chloride, becoming itself converted into sulphur dioxide, sulphate, nitrous oxide, and water. Mercuric nitrate oxidises hydroxyamidosulphate more completely, but ferric chloride seems to act like copper sulphate, and liberates sulphur dioxide.

An alkali hydroximidosulphate is also decomposed by copper sulphate, but not so easily, for it can be heated with it at 100° for a short time without change, and only decomposes (but then suddenly) some degrees above that temperature, yielding the products which a hydroxyamidosulphate gives, together with sulphuric acid coming from its hydrolysis into that salt.

Although the presence of much sulphuric acid prevents the action of copper sulphate on a hydroxyamidosulphate, the acid in moderate excess has but little effect.

Sodium hydroximidosulphate, if kept with care, decomposes only very slowly in a way which has hitherto been obscure (Trans., 1894, 65, 541), but if considered in connection with the action of copper sulphate it may be regarded as essentially the same as that brought about by heating it, in solution, with that salt. For, the decomposed hydroximidosulphate contains, besides acid sulphate and hydroxyamidosulphate, both a little gas (nitrous oxide or nitrogen) shut up in its pores which escapes when the mass is dissolved in water, and also a little amidosulphate, which can be separated from the other salts by precipitation with mercuric nitrate (Trans., 1896, 69, 1649, also 1640,

The decomposition of hydroxyamidosulphates by copper sulphate is

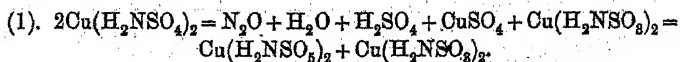


also in evident relation with the gradual decomposition of impure hydroxylamine hydrochloride, particularly when ferric chloride is among the impurities, water, nitrous oxide, and ammonia (in place of amidosulphuric acid) being the principal, if not the sole, products.

There is a very marked difference between a hydroxyamidosulphate and a hydroximidosulphate in the relative proportions of the several products of decomposition, but this seems to be owing merely to the fact that the temperature of the decomposition is different, for according as hydroxyamidosulphate is heated slowly or rapidly the proportions of the products of decomposition deviate from or approach those which obtain when a hydroximidosulphate is decomposed, this only taking place at a temperature above  $100^{\circ}$ .

As little as one-tenth of an equivalent of copper sulphate has been found to suffice for the complete decomposition of an alkali hydroxyamidosulphate, the copper sulphate not being consumed in the change it effects; this allows of the decomposition being to a great extent carried out at the boiling temperature, when again the result approaches that observed where hydroximidosulphate is the salt decomposed. Although much less than the amount above named will effect an almost complete decomposition, the quantity of the catalytic agent cannot be very greatly reduced; this seems to be due in part to the simple hydrolysis of some of the hydroxyamidosulphuric acid set free by the sulphuric acid arising from the decomposition of another portion of the salt by the copper sulphate during the prolonged heating which is then necessary.

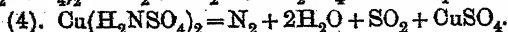
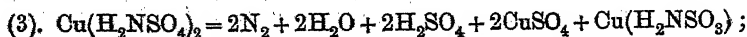
Since the cupric salt suffers no reduction, it will be seen that one part of the hydroxyamidosulphate becomes reduced to amidosulphate by yielding oxygen for the oxidation of the other part to water, sulphate, and nitrous oxide. The following equation shows that the hydroxyamidosulphate may change by cumulative resolution, half into a reduced product (amidosulphate), and half into oxidised products together equivalent to the non-existent dihydroxyamidosulphate:



Such an equation expresses much of what happens in the decomposition of a hydroxyamidosulphate at a lower temperature, but even in this case, and much more so in the decomposition of a hydroximidosulphate by copper sulphate, where the temperature is higher, a third molecule decomposes in another way. The result is that the free sulphuric acid shown in the above equation gets neutralised, and the third molecule of hydroxyamidosulphuric acid yields neither sulphate nor amidosulphate, all its sulphur being eliminated as dioxide, its nitrogen as

nitrous oxide, and its hydrogen as water, thus reverting to sulphurous and hyponitrous acids, just as it does under the influence of an alkali (p. 978). Adding to equation (1) that of  $\text{Cu}(\text{H}_2\text{NSO}_4)_2 = \text{N}_2\text{O} + 2\text{H}_2\text{O} + 2\text{SO}_2 + \text{CuO}$ , we get (2),  $3\text{Cu}(\text{H}_2\text{NSO}_4)_2 = 2\text{N}_2\text{O} + 4\text{H}_2\text{O} + 2\text{SO}_2 + 2\text{CuSO}_4 + \text{Cu}(\text{H}_2\text{NSO}_3)_2$ , with products free from acid.

It is possible to express the decomposition of hydroxyamidodisulphate differently, by making nitrogen one of the products in place of nitrous oxide, thus:



In (3), sulphur dioxide is not a product, whilst in (4) it is. Whether, however, nitrogen is formed, even in small quantity, is doubtful. Along with the nitrous oxide, soluble in alcohol, we found a little insoluble gas—about 4 per cent. by volume of the whole gas,—but we are not prepared to assert that this was not due to air, in spite of the precautions we took to expel all air from the apparatus by carbon dioxide before the decomposition. It will be seen from the equations that, with nitrous oxide as a product of the decomposition, the sulphur appearing as sulphate equals that as amidodisulphate, whereas, with nitrogen as a product, the sulphur as sulphate is double that as amidodisulphate in (3), whilst in (4) there is none as amidodisulphate. Now, in the observed decompositions of hydroxyamidodisulphate the sulphur as sulphate has been found equal, on the average, to that as amidodisulphate, a result showing that, within the limits of accuracy of the somewhat complex analytical work, no nitrogen is generated.

Although, when using copper sulphate or copper hydroxyamidodisulphate, no change to cuprous salt is observable, the reduction of cupric chloride to cuprous chloride points clearly to the activity of the copper salt as a 'carrier of oxygen' from one molecule of the hydroxyamidodisulphate to another.

#### *Results of the Quantitative Experiments and Method Employed.*

The results of the experiments are given, not in the order in which they were obtained, but in that of the growth in quantity of the sulphur dioxide produced.

In an experiment in which copper hydroxyamidodisulphate was heated very slowly, so as to carry out the decomposition at as low a temperature as possible (boiling the solution only at the end in order to expel the last portions of sulphur dioxide), results were obtained which agree sufficiently well with those calculated on the assumption that 2.7 per cent. of the salt gives all its sulphur as dioxide, its hydrogen as water, and its nitrogen as nitrous oxide, whilst the rest of the salt decomposes according to equation (1):

	Sulphur as dioxide.	trioxide and amidosulphate.
Found .....	3.5	96.2
Calc. ....	3.7	96.3

An experiment with sodium hydroxyamidosulphate and its equivalent of copper sulphate gave results indicating that about 5.3 per cent. yielded all its sulphur as dioxide, the rest of the salt giving sulphur trioxide (sulphate, sulphuric acid) and amidosulphate (equation 1):

	dioxide.	Sulphur as trioxide.	amidosulphate.	acidity.
Found .....	5.5	46.0	48.0	21.6
Calc. ....	5.3	47.4	47.4	21.0

Copper hydroxyamidosulphate, in four experiments, gave results agreeing nearly with the assumption that 13.2 per cent. of the salt gave sulphur dioxide, the rest decomposing according to equation (1):

	dioxide.	Sulphur as trioxide.	amidosulphate.	acidity.
Found.....	13.0	43.0	43.6	11.1
„ .....	13.0	43.3	43.2	
„ .....	13.1	86.6		
„ .....	13.3	86.5		
Calc. ....	13.2	43.4	43.4	15.1

In another experiment, copper hydroxyamidosulphate gave the following results, as against calculation for 15.4 per cent. to decompose so as to yield its sulphur as dioxide:

	dioxide.	Sulphur as trioxide.	amidosulphate.	acidity.
Found.....	15.1	42.9	41.6	10.7
Calc. ....	15.4	42.3	42.3	13.5

In one more trial, copper hydroxyamidosulphate decomposed nearly as if 16.6 per cent. of it yielded all of its sulphur as dioxide:

	dioxide.	Sulphur as trioxide and amidosulphate.	acidity.
Found .....	16.3	83.3	9.3
Calc. ....	16.6	83.4	12.5

A solution of potassium hydroximidosulphate, heated with very little more than its equivalent of copper sulphate, gave results showing that 25 per cent. of the salt yielded all the sulphur of the hydroxyamidosulphate, coming from it by hydrolysis, as sulphur dioxide:

	dioxide.	Sulphur as trioxide.	amidosulphate.	acidity.
Found .....	25.2	37.3	37.0	5.5
Calc. ....	25.0	37.5	37.5	6.25

A solution containing sodium hydroximidosulphate and copper sulphate decomposed, in two experiments, in such a way that about 28 per cent. of the hydroxyamidosulphate sulphur became dioxide.

	dioxide.	trioxide.	Sulphur as amidosulphate.	acidity.
Found .....	27.6	36.9	35.0	4
" .....	28.0	36.2	35.8	5.8
Calc. ....	28.0	36.0	36.0	4

The numbers in the above table stand for parts per hundred of the sulphur of the total hydroxyamidosulphate decomposed, and not of the sulphur of the hydroximidosulphate even when this salt has been that experimented with. The 'acidity' sulphur is calculated as if the acidity is due to sulphuric acid, not amidosulphuric acid. The 'trioxide' sulphur is that of the sulphuric acid and copper sulphate yielded by the decomposition. The differences between the calculated quantities and those found must be largely attributed to imperfect estimation; they cannot be due to error in theory, because no explanation of the change other than that adopted is possible. In a copper-salt solution mixed with much barium sulphate, it was not easy to titrate acid with litmus as indicator. The separation of sulphate and amidosulphate is not a simple process, especially when much sulphate is present derived from sources other than the reaction to be dealt with.

The salt employed in the experiments was either copper hydroxyamidosulphate, or sodium hydroxyamidosulphate with copper sulphate, or one of the alkali hydroximidosulphates with copper sulphate.

1. A solution of the copper salt, containing only a very little copper sulphate, was prepared from normal barium hydroxyamidosulphate and copper sulphate; the barium salt (*Trans.*, 1889, 55, 762, 764) had to be prepared as wanted, because of the instability of the hydroxyamidosulphates. The strength of the solution was determined by a barium estimation (hydrolysis in sealed tube and weighing of the barium sulphate). Copper sulphate in slight excess, and carefully weighed, was added to the weighed solution of the barium salt, and the copper hydroxyamidosulphate at once used without filtering off the barium sulphate.

2. Sodium hydroxyamidosulphate solution was prepared just before use by hydrolysing a centigram-molecule of the hydroximidosulphate by adding to its solution a minute and known quantity of sulphuric acid (*Trans.*, 1899, 75, 79), and then half a centigram-molecule of copper sulphate.

3. Potassium or sodium hydroximidosulphate in the quantity of a centigram-molecule was dissolved and directly heated with a half molecule, in centigrams, of copper sulphate.

The solution (either 1, 2, or 3) contained in a small flask connected with a tube receiver holding bromine water kept cold, was heated, sometimes quickly, sometimes slowly, either by a spirit lamp or in a bath of sulphuric acid, the solution being finally boiled for some minutes, so as to drive all sulphur dioxide into the bromine water. Before heating, air was removed from the apparatus by a current of carbon dioxide. In one experiment, the apparatus was made entirely of glass. The oxidised sulphur dioxide was weighed as barium sulphate.

The boiled-out copper solution was titrated with *N*/10 soda (free from sulphate), using litmus as indicator. The imperfection of this operation was proved beyond doubt on calculating out the nature of the changes which had occurred, but it was serviceable and the best available under the circumstances.

To the boiling hot solution and precipitate of barium sulphate, barium chloride was added in excess, the total precipitate collected, well washed, and transferred to a pressure tube, in which it was heated with hydrochloric acid for some hours at 150°. The barium sulphate, after being again washed on the filter, was ignited and weighed. The second filtrate and washings contained sulphuric acid, the quantity of which was estimated as barium salt. To make this part of the analytical process intelligible, it must be explained that barium amidosulphate, although itself quite soluble in water, is partially precipitated along with barium sulphate even in presence of hydrochloric acid (*Trans.*, 1896, 69, 1615). At 150°, the precipitated amidosulphate hydrolyses, yielding barium sulphate and ammonium sulphate in molecular proportion.

The copper filtrate from the crude barium precipitate was evaporated to a small volume, heated with hydrochloric acid for some hours at 150°, and mixed with barium chloride. The precipitated barium sulphate represented the principal quantity of amidosulphate sulphur, the full amount of which was ascertained by adding to it twice the quantity of that in the ammonium sulphate extracted by hydrolysis from the crude barium precipitate. The sulphur from the hydroxyamidosulphate, obtained as sulphate, was found by subtracting from the total the sum of the quantities of sulphur present as (a) copper sulphate taken; (b) barium sulphate from the hydrolysed barium amidosulphate which had been precipitated along with the barium sulphate by barium chloride; (c) sulphuric acid added for hydrolysing the hydroximidosulphate, when that salt had been started with; and (d) in the same case, sulphuric acid resulting from the hydrolysis of the hydroximidosulphate to hydroxyamidosulphate.

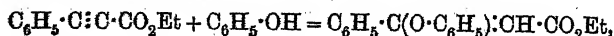
Hardly any attempt was made to estimate the amount of nitrous oxide liberated. To do so would only have been useful as a check on

the accuracy of the determinations of the amidosulphate, and for that purpose the two substances would have had to be estimated in the products of one experiment. This, it did not seem possible to do. An experiment in which hydroxyamidosulphate was decomposed gave 55.3 per cent. of the nitrogen as nitrous oxide, as against 56.6 calculated from the equation most in accordance with amidosulphate and other sulphur determinations. The method of measuring the nitrous oxide and nitrogen was to expel air from the apparatus by a current of carbon dioxide continued for some time, and then to heat the copper salt and boil out the gases, these being collected over mercury and potassium hydroxide, and measured. The alkali was then replaced by absolute alcohol to dissolve the nitrous oxide, and the residual gas measured.

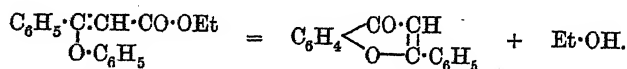
LXXXVIII.—*Condensation of Phenols with Esters of the Acetylene Series. Part I. Action of Phenols on Ethyl Phenylpropionate.*

By SIEGFRIED RUHEMANN and FRED. BEDDOW, D.Sc., Ph.D.

FROM the results arrived at by one of us and his pupils in the course of researches on the esters of the acetylene series, we have been induced to study the reactions of these esters with the phenols. This investigation appeared to be of especial interest as it was hoped that ethyl phenylpropionate would unite with the sodium phenolates in the following manner:



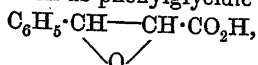
and yield ethyl  $\beta$ -phenoxycinnamate and its homologues, which in turn might be converted into flavone and its derivatives according to the equation,



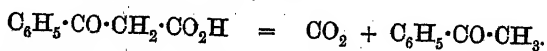
Thus a synthesis of the group of substances standing in close relationship to the yellow plant dyes was indicated, which would have the advantage of greater simplicity over that elaborated by von Kostanecki and his pupils (*Ber.*, 1898, 31, 696, 705, 1757).

We have proved that the aryl derivatives of ethyl  $\beta$ -hydroxycinnamate are readily formed, but as yet we have not succeeded in effecting their condensation to the flavones. Our attention, for the present, has been chiefly directed to the investigation of the compounds which are produced by the union of ethyl phenylpropionate

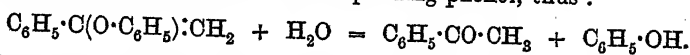
with the sodium phenolates. These must be regarded as ethers of  $\beta$ -hydroxycinnamic acid, and are therefore isomeric with the corresponding compounds of  $\alpha$ -hydroxycinnamic acid which have been obtained by Ogialoro and his pupils.  $\alpha$ -Hydroxycinnamic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$ , or its tautomeride, benzylglyoxylic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , as well as phenylglycidic acid,



readily lose carbon dioxide and yield  $\alpha$ -toluylaldehyde. On the other hand,  $\beta$ -hydroxycinnamic acid,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , or its tautomeride, benzoylactic acid,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , decomposes into carbon dioxide and acetophenone, thus:



We find that the aryl ethers of  $\beta$ -hydroxycinnamic acid, which are obtained from their ethyl esters by hydrolysis with alcoholic potash, undergo the latter transformation, but that phenoxystyrene,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}_2$ , and its homologues are formed as intermediate products; these readily decompose when digested with dilute acid, yielding acetophenone and the corresponding phenol, thus:



These changes take place most readily in the case of the naphthyl ethers of  $\beta$ -hydroxycinnamic acid, for if the acids remain in contact with dilute sulphuric acid at the ordinary temperature for some time, a gradual evolution of carbon dioxide occurs and acetophenone is formed.

The experiments recorded in this paper deal with the study of the ethyl esters which are produced by the union of phenol, *o*- and *p*-cresol, and  $\alpha$ -naphthol with ethyl phenylpropiolate. Our next paper will contain a description of the corresponding compounds which are formed from the product of the interaction of *m*-cresol and the ester, as well as the results of our investigations on the behaviour of phenols towards ethyl acetylenedicarboxylate.

It may be mentioned that the chief object of our research, namely, the condensation of the aryl ethers of  $\beta$ -hydroxycinnamic acid to members of the flavone group, has not been lost sight of, and that experiments are in progress in order to accomplish this task.

#### EXPERIMENTAL.

*Ethyl  $\beta$ -Phenoxycinnamate*,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}\cdot\text{CO}_2\text{C}_2\text{H}_5$ .

The union of sodium phenolate with ethyl phenylpropiolate takes place very slowly at the ordinary temperature, only a small quantity

of the additive product being formed when dry phenolate suspended in absolute ether has been left in contact with the ester for six days. The reaction, however, proceeds much more readily, and the yield is increased to 80—90 per cent. of the calculated quantity of ethyl  $\beta$ -phenoxy-cinnamate, when the following method is adopted. Metallic sodium (1 at.) is dissolved in an excess of hot phenol, and, after standing until the phenolate has separated, ethyl phenylpropiolate (1 mol.) is gradually added to the still warm magma; the phenolate enters into solution, whilst the temperature rises and a dark oil is formed, which on cooling sets to a semi-solid mass. This is well shaken with dilute sulphuric acid and ether, during which process the viscous product entirely disappears. After the excess of phenol has been removed by frequently agitating the ethereal layer with dilute caustic potash solution, the ether is dried with calcium chloride, evaporated, and the remaining oil distilled in a vacuum; it boils at 204—205° under 10 mm. pressure. On analysis:

0.2143 gave 0.5965  $\text{CO}_2$  and 0.1205  $\text{H}_2\text{O}$ .  $\text{C} = 75.91$ ;  $\text{H} = 6.24$ .

$\text{C}_{17}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 76.11$ ;  $\text{H} = 5.97$  per cent.

The ester is a colourless, odourless, viscous oil which after standing for some days gradually solidifies to a mass of crystals which is readily dissolved by ether or hot alcohol and on recrystallisation from light petroleum (b. p. 60—65°) yields prisms melting at 73—74°.

On analysis, these crystals gave numbers which agree with those obtained in the case of the oil:

0.1826 gave 0.5980  $\text{CO}_2$  and 0.1008  $\text{H}_2\text{O}$ .  $\text{C} = 75.87$ ;  $\text{H} = 6.13$  per cent.

Although the ester does not melt below 73—74°, it remains liquid for a long time after distillation and solidifies slowly even after a crystal is placed in the oil. A similar phenomenon is experienced with ethyl  $\beta$ -*p*-cresoxycinnamate, whilst the corresponding esters obtained from *o*-cresol and  $\alpha$ -naphthol have up to the present shown no sign of solidifying, although prepared some weeks ago.

$\beta$ -Phenoxy-cinnamic acid,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_5) : \text{CH} \cdot \text{CO}_2\text{H}$ , is obtained by digesting its ester with alcoholic potash on the water-bath for 2 hours; after evaporating off the alcohol and adding water, a clear solution is obtained from which sulphuric acid precipitates an oil. This solidifies on standing a short time, and when recrystallised from dilute alcohol colourless needles are obtained which soften at about 125° and melt at 143° with evolution of gas. On analysis:

0.2256 gave 0.6197  $\text{CO}_2$  and 0.1040  $\text{H}_2\text{O}$ .  $\text{C} = 74.95$ ;  $\text{H} = 5.12$ .

$\text{C}_{15}\text{H}_{12}\text{O}_3$  requires  $\text{C} = 75.0$ ;  $\text{H} = 5.0$  per cent.

$\beta$ -Phenoxy-cinnamic acid is sparingly soluble in boiling water, but



readily so in alcohol or chloroform, and dissolves with the greatest ease in ether.

The *silver* salt is obtained as a white precipitate on adding silver nitrate to a solution of the acid in dilute ammonia; it is only slightly soluble in cold water, exposure to light has little effect on it, and it can be dried at 100° without change. On analysis:

0.3315 left, on ignition, 0.1030 Ag. Ag = 31.07.

$C_{15}H_{11}O_3Ag$  requires Ag = 31.12 per cent.

*Phenoxystyrene*,  $C_6H_5 \cdot C(O \cdot C_6H_5) : CH_2$ .—As already mentioned,  $\beta$ -phenoxycinnamic acid decomposes on heating, carbon dioxide being evolved, and nearly the theoretical quantity of phenoxystyrene being formed. This compound boils at 151° under 14 mm. pressure; it is a colourless oil with an aromatic odour, and has the density  $d_{17^\circ/17^\circ}$  1.10729. On analysis:

0.1957 gave 0.6160  $CO_2$  and 0.1075  $H_2O$ . C = 85.84; H = 6.10.

$C_{14}H_{12}O$  requires C = 85.71; H = 6.12 per cent.

When bromine is added to phenoxystyrene, a violent reaction takes place, the whole becoming black, and hydrogen bromide being evolved. This gas is also evolved when carbon tetrachloride is used as a diluent, although the action in this case proceeds quietly; the oily product, however, decomposes on distillation in a vacuum. When phenoxystyrene is heated with dilute hydrochloric acid, acetophenone and phenol are formed; this was proved by shaking up the mixture with caustic potash to remove the phenol, then identifying the acetophenone, isolated from the remaining oil, by its boiling point and characteristic odour. On analysis:

0.1816 gave 0.5315  $CO_2$  and 0.1080  $H_2O$ . C = 79.82; H = 6.60.

$C_8H_8O$  requires C = 80.0; H = 6.66 per cent.

The presence of phenol in the alkaline solution was verified by the ordinary tests.

*Ethyl  $\beta$ -o-cresoxycinnamate*,  $C_6H_5 \cdot C(O \cdot C_6H_4 \cdot CH_3) : CH \cdot CO_2C_2H_5$ .

This compound is formed from ethyl phenylpropiolate and sodium *o*-cresolate in the same manner as ethyl phenoxycinnamate; it is a colourless, odourless oil which boils at 212—213° under 10 mm. pressure, and has not been obtained in the solid form. On analysis:

0.1805 gave 0.5062  $CO_2$  and 0.1041  $H_2O$ . C = 76.48; H = 6.40.

$C_{18}H_{18}O_3$  requires C = 76.59; H = 6.38 per cent.

The hydrolysis of ethyl  $\beta$ -*o*-cresoxycinnamate readily takes place on boiling with alcoholic potash for an hour. After most of the

alcohol has been removed by evaporation on the water-bath, the alkaline liquor is diluted with water and sulphuric acid added to the clear solution. This precipitates  $\beta$ -*o*-cresoxycinnamic acid,  $C_6H_5 \cdot C(O \cdot C_6H_4 \cdot CH_3) : CH \cdot CO_2H$ , as an oil, which after a short time sets to a solid mass. The acid dissolves with great ease in alcohol or chloroform, very freely in ether, but only sparingly in boiling water. After being crystallised from dilute alcohol, it is obtained in colourless plates which melt at  $133-134^\circ$  with evolution of carbon dioxide. On analysis:

0.2047 gave 0.5665  $CO_2$  and 0.1026  $H_2O$ .  $C = 75.47$ ;  $H = 5.56$ .

$C_{16}H_{14}O_3$  requires  $C = 75.59$ ;  $H = 5.51$  per cent.

The *silver* salt is obtained as a white precipitate on adding silver nitrate to the solution of the acid in ammonia. On analysis:

0.2992 left, on ignition, 0.0893 Ag.  $Ag = 29.84$ .

$C_{16}H_{13}O_3Ag$  requires  $Ag = 29.91$  per cent.

*o*-Cresoxystyrene,  $C_6H_5 \cdot C(O \cdot C_6H_4 \cdot CH_3) : CH_2$ — $\beta$ -*o*-Cresoxycinnamic acid, on heating, decomposes quantitatively into carbon dioxide and *o*-cresoxystyrene; this substance is a colourless oil which boils at  $158^\circ$  under 10 mm. pressure; it is insoluble in water, but readily dissolves in alcohol or ether, and has the density  $d_{19^\circ/19^\circ} 1.0554$ . On analysis:

0.1953 gave 0.6133  $CO_2$  and 0.1173  $H_2O$ .  $C = 85.64$ ;  $H = 6.67$ .

$C_{15}H_{14}O$  requires  $C = 85.70$ ;  $H = 6.67$  per cent.

On digesting with dilute hydrochloric acid, the *o*-cresyl ether of hydroxystyrene, like the corresponding phenoxystyrene, is hydrolysed with the greatest ease, and yields acetophenone and *o*-cresol. These have been separated in the usual way, and identified as such by their boiling points and chemical behaviour.

*Ethyl- $\beta$ -o-cresoxycinnamate*,  $C_6H_5 \cdot C(O \cdot C_6H_4 \cdot CH_3) : CH \cdot CO_2C_2H_5$ .

For the preparation of this ester, the same method was used as in the previous case; the fact that the cresolate surrounds the metallic sodium and prevents it from dissolving readily necessitates prolonged heating and the use of a large excess of the cresol in this case. The difficulty was overcome, however, by digesting the metal with a mixture of cresol and toluene until it had dissolved. On adding ethyl  $\beta$ -phenylpropionate to the hot magma, the whole liquefies and on cooling sets to a semi-solid mass. This is shaken with dilute sulphuric acid and ether, and after removal of the excess of the cresol and subsequent evaporation of the ether, an oil was obtained which distils at  $216-217^\circ$  under 10 mm. pressure. The quantity of the pure ester

obtained amounted to 80 per cent. of that required by theory. On analysis :

0.1963 gave 0.5509  $\text{CO}_2$  and 0.1130  $\text{H}_2\text{O}$ .  $\text{C}=76.53$ ;  $\text{H}=6.39$ .

$\text{C}_{18}\text{H}_{18}\text{O}_3$  requires  $\text{C}=76.59$ ;  $\text{H}=6.38$  per cent.

Ethyl- $\beta$ -*p*-cresoxycinnamate, when redistilled, is a colourless, odourless, viscous oil which, after standing for some days, begins to crystallise in needles melting, not quite sharply, at  $73^\circ$ .

$\beta$ -*p*-Cresoxycinnamic acid,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3)\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , is obtained on hydrolysis of the ester by means of alcoholic potash, and is precipitated as an oil which solidifies after a short time, when dilute sulphuric acid is added to the alkaline solution. In its solubility and chemical behaviour, it resembles the esters previously described; it crystallises from hot dilute alcohol in colourless needles which melt and decompose at  $136$ — $137^\circ$ . On analysis :

0.1900 gave 0.5260  $\text{CO}_2$  and 0.0947  $\text{H}_2\text{O}$ .  $\text{C}=75.50$ ;  $\text{H}=5.53$ .

$\text{C}_{18}\text{H}_{14}\text{O}_3$  requires  $\text{C}=75.59$ ;  $\text{H}=5.51$  per cent.

The silver salt, dried at  $100^\circ$ , was also analysed :

0.2605 left, on ignition, 0.0778 Ag.  $\text{Ag}=29.86$ .

$\text{C}_{16}\text{H}_{13}\text{O}_3\text{Ag}$  requires  $\text{Ag}=29.91$  per cent.

*p*-Cresoxystyrene,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3)\cdot\text{CH}_2$ , is obtained by heating the acid; it is a colourless oil having an aromatic odour; it boils at  $162$ — $163^\circ$  under 10 mm. pressure, and has the density  $d_{16^\circ/16^\circ}$  1.0514. On analysis :

0.1918 gave 0.6006  $\text{CO}_2$  and 0.1167  $\text{H}_2\text{O}$ .  $\text{C}=85.40$ ;  $\text{H}=6.75$ .

$\text{C}_{15}\text{H}_{14}\text{O}$  requires  $\text{C}=85.71$ ;  $\text{H}=6.67$  per cent.

*p*-Cresoxystyrene is decomposed by boiling with hydrochloric acid, and yields acetophenone and *p*-cresol.

Ethyl  $\beta$ - $\alpha$ -Naphthoxycinnamate,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_{10}\text{H}_7)\cdot\text{CH}\cdot\text{CO}_2\text{C}_2\text{H}_5$ .

$\alpha$ -Naphthol (1 mol.) is added to the solution of sodium (1 at.) in absolute alcohol, the alcohol removed by heating the solution in a vacuum at  $100^\circ$ , and the dry naphtholate digested with ethyl  $\beta$ -phenylpropionate (1 mol.), dissolved in toluene, for 4 hours on the water-bath. The product is treated with dilute sulphuric acid, then with caustic potash, and the oil which remains after evaporation of the toluene fractionated under diminished pressure. Almost the total quantity distils over at  $270^\circ$  under 16 mm. pressure as a yellowish oil which, at the ordinary temperature, has the consistency of Canada balsam. On analysis :

0.1953 gave 0.5684  $\text{CO}_2$  and 0.1007  $\text{H}_2\text{O}$ .  $\text{C}=79.37$ ;  $\text{H}=5.73$ .

$\text{C}_{21}\text{H}_{18}\text{O}_3$  requires  $\text{C}=79.24$ ;  $\text{H}=5.66$  per cent.

$\beta$ -*Naphthoxycinnamic acid*,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_{10}\text{H}_7)\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , is obtained on hydrolysis of the ethyl ester by means of alcoholic potash, and is thrown down as a resinous product on adding dilute sulphuric acid to the alkaline liquor after dilution with water; the resin dissolves freely in sodium carbonate, yielding a cloudy, reddish solution which is decolorised by animal charcoal. An excess of a mineral acid precipitates from the filtrate a whitish solid, which is scarcely soluble in water, but readily dissolves in ether; after being crystallised from alcohol, it is obtained in groups of colourless needles, and melts and decomposes at  $152-153^\circ$ . On analysis:

0.1990 gave 0.5716  $\text{CO}_2$  and 0.0875  $\text{H}_2\text{O}$ .  $\text{C}=78.33$ ;  $\text{H}=4.88$ .

$\text{C}_{19}\text{H}_{14}\text{O}_3$  requires  $\text{C}=78.62$ ;  $\text{H}=4.83$  per cent.

The solution of the acid in ammonia gives, with silver nitrate, a white *silver salt* which is stable at  $100^\circ$ . A silver determination furnished the following result:

0.2980 left, on ignition, 0.0815 Ag.  $\text{Ag}=27.34$ .

$\text{C}_{19}\text{H}_{13}\text{O}_3\text{Ag}$  requires  $\text{Ag}=27.20$  per cent.

$\beta$ -*Naphthoxycinnamic acid* on heating loses carbon dioxide and yields a yellowish oil which boils at  $212^\circ$  under 10 mm. pressure. This has not been further examined, but there cannot be any doubt that it is  $\alpha$ -naphthoxystyrene.

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CAMBRIDGE.

### LXXXIX.—*Estimation of Furfuraldehyde.*

By WILLIAM CORMACK.

THE most reliable method for estimating this aldehyde is that of Flint and Tollens (*Landw. Versuchs-Station*, 1893, 42, 381), which is based on the production and gravimetric estimation of the phenylhydrazone. Their method, however, involves the use of a factor, which must be determined for the special conditions under which the estimation is carried out, as it varies with the concentration of the solution, amount of substance, &c. Further, since the phenylhydrazone cannot be heated above  $60^\circ$ , the time required to dry it to constant weight may amount to from one to three days, according to the means and apparatus available. The following method dispenses with the use of a factor, and can be carried out in half an hour with a much

smaller quantity of substance than is necessary for the successful application of the phenylhydrazone process.

The method is based on the oxidation of furfuraldehyde to pyromucic acid by means of an ammoniacal solution of silver oxide, the reaction being represented by the equation



Under the conditions given, this reaction takes place quantitatively, so that the estimation of furfuraldehyde may be reduced to the volumetric estimation of silver.

A solution of ammoniacal silver oxide is prepared by precipitating a known weight of silver nitrate by means of caustic soda solution, thoroughly washing the silver oxide with water, and dissolving it in the minimum quantity of ammonia solution. The solution is then diluted to decinormal strength and standardised according to Volhard's method by means of decinormal ammonium thiocyanate.

The following results were obtained with a solution of pure furfuraldehyde which contained 2.50 grams of furfural in the litre. In each case, 10 c.c. of the furfuraldehyde solution containing 0.0250 gram of furfuraldehyde were added to 10 c.c. of the silver solution, and the mixture warmed at 25° for the times given in the subjoined table. The precipitated silver was then removed by filtration through asbestos, the filtrate acidified with nitric acid, and titrated with decinormal ammonium thiocyanate solution:

Time of heating.	AmSCN required.	Ag <sub>2</sub> O reduced.	Furfuraldehyde found.
13 min.	5.0 c.c.	5.0 c.c.	0.0240 gram.
19	4.9	5.1	0.0245
26	4.8	5.2	0.0250
32	4.8	5.2	0.0250
39	4.8	5.2	0.0250
45	4.8	5.2	0.0250

From this table, it is apparent that after the furfuraldehyde has been oxidised there is no further action on the silver solution, so that the time of heating is immaterial so long as it is sufficient to permit complete oxidation. At 25°, half an hour is necessary, but at 70° only a few minutes are required.

The filtrate from the precipitated silver gave, on acidification and treatment with ether, an ethereal extract, which, after evaporation of the ether, left a crystalline residue possessing the melting point and other properties of pyromucic acid.

An ammoniacal solution of silver nitrate, such as was employed by Henderson in the estimation of sugars (Trans., 1896, 69, 145), cannot

be substituted for the ammoniacal solution of silver oxide in the estimation of furfuraldehyde.

*Application of the Method to Furfuraldehyde Solutions obtained from Textile Fibres, Sugars, &c.*—The vegetable substance is distilled with 10 per cent. hydrochloric acid until furfuraldehyde no longer passes over in the distillate (Flint and Tollens, *loc. cit.*; Cross and Bevan, *Cellulose*, p. 99). The volume of the distillate is measured, and the whole, or a known fraction of it, neutralised with solid sodium carbonate. A small quantity of oxalic acid is then added, and the solution distilled with steam. The distilling flask must be provided with a trap bulb, otherwise chlorides pass over into the distillate. The distillation is continued until a drop of the distillate no longer gives a red coloration with a solution of aniline acetate. Excess of ammoniacal silver solution is now added to the distillate, and the mixture heated to 60–70°. The form in which the reduced silver separates varies according to the strength of the furfuraldehyde solution. A mirror is frequently formed on the walls of the containing vessel, but occasionally the silver remains suspended in the colloidal condition, and cannot be filtered off. In such a case, it is necessary to cool the reduced solution and then add a few c.c. of 25 per cent. solution of caustic potash to induce coagulation. The caustic potash used must of course be free from chlorides. The silver is then filtered off and the filtrate acidified and titrated with ammonium thiocyanate as before.

The following results were obtained by this method:

A sample of jute (distilled under special conditions so as to obtain the maximum yield of furfuraldehyde) yielded 500 c.c. of distillate. Of this distillate, 400 c.c. were treated by the phenylhydrazine method of Flint and Tollens, and 100 c.c. by the silver method as above described.

Phenylhydrazine method ...furfuraldehyde=10.9 per cent.

Silver method..... " =10.7 "

By the phenylhydrazine method, Smith (Trans., 1894, 65, 479) found the percentage of furfuraldehyde from oat-straw cellulose to be 14.5. Two samples treated by the silver method gave respectively 14.4 and 14.8 per cent.

The silver method, then, with pure solutions of furfuraldehyde gives accurate results, and also results for celluloses, &c., which are comparable with those obtained by the phenylhydrazine method. The advantages it possesses over this method are that a much smaller quantity of material need be used for the estimation, and that the time required in the actual determination of furfuraldehyde in a hydrochloric acid distillate is reduced from a day to half an hour.





*C. Friedel*



## FRIEDEL MEMORIAL LECTURE.

By J. M. CRAFTS, Professor.

THE tomb of Friedel at Montauban bears the inscription :

CHARLES FRIEDEL

né à Strasbourg le 12 Mars 1832

décédé à Montauban le 20 Avril 1899.

Membre de l'Institut.

"Le juste vivra par la foi

La mémoire du juste sera en bénédiction."

So far as a tombstone can bear faithful witness to a life, this short description is true of a man who chose science for his occupation, and strove to do his duty towards God and man with keen observation of things temporal and a simple faith in things eternal.

We, as members of the Chemical Society, are chiefly concerned with his contributions to science, but enumeration of these will not be complete unless it is said that high among his contributions to the advancement of science stands the influence of a very beautiful character and of a well-balanced judgment upon the men of his time, even extending beyond his own nation, and during the excited period after the French national disaster, serving as a connecting link between the scientific reasoning of his countrymen and the spread of philosophy abroad.

The influence of individuals and of schools upon the patronage of the younger men for educational positions is peculiarly important in France. The destiny of a student of science depends greatly upon the leader whom he chooses to follow, and there is sufficient cohesion among the members of a school to make it an effective body. That founded by Wurtz was continued by Friedel, who was the oldest of the French followers of Wurtz, and only fifteen years younger than his leader. His immediate associates were Gautier, Grimaux, Salet, Lebel, and, later, Hanriot and the Combes. With Friedel, as with Wurtz, charm of character, as well as scientific talent, contributed to enlarge this group of men, bound together by a common regard and by community of views, until the school became an important factor in the nation's progress.

One of the most notable channels through which scientific patronage is exercised is in the Academy of Science, whose organisation offers very effective means of exerting influence in the election of new members, in the appointment to professional places, in the annual distribu-

tion of large numbers of prizes, and in the examination by committees of questions of scientific, and sometimes of national, interest. Friedel played an important part in this work, and his competency in chemistry, mineralogy, and mathematics, together with his evident fair-mindedness, gave great weight to his opinion among his colleagues.

There is much significance in the way in which the title, Member of the Institute, is used as the only record of occupation placed upon Friedel's gravestone, and it is quite in accord with French usage to consider this distinction one of the highest that the nation can bestow; thus Napoleon, in familiar letters, having nothing to do with science, signs himself, "Bonaparte, Général en Chef, Membre de l'Institut."

The circumstances of Friedel's family, as well as his subsequent position, favoured the development of his scientific career. His childhood, passed at Strasbourg, brought him, even during school years, in contact with men of science, and his inclination for scientific studies was favoured by his parents.

He took his Bachelor's degree in letters in 1849, and that in science in 1850. He then entered his father's counting-house, and while there had an opportunity of attending lectures by Pasteur, Daubrée, Bertin, and Lereboullet at Strasbourg University. His stay in the counting-house lasted only a year, and, as might have been expected, the attractions of science presented by such men drew him away from commerce.

In 1851, he went to Paris to live with his maternal grandfather, G. L. Duvernoy, Professor at the Collège de France and the Museum of Natural History. He took the Licentiate degree in mathematics at the Sorbonne in 1854, and that in physical science July 7th, 1855. While pursuing these studies, he commenced research work at the Museum, and a letter, dated December 21st, 1854, speaks of the discovery of two new faces in crystals of corundum, given him for examination by Dufrénoy (he had refused a place of assistant with that mineralogist), and also of a research confided to him by Wurtz.

He followed the lectures of Senarmont at the School of Mines, and formed a strong personal attachment to him while engaged in mineralogical studies under his guidance. In 1856, Friedel was appointed Curator of the mineralogical collection of the School of Mines, then under the direction of Dufrénoy, and for the remainder of his life was actively occupied with enriching that important collection. He was at first attracted by the crystallographical side of mineralogy, and then towards optics, until, at the suggestion of Senarmont, he thought of devoting himself to mathematics and becoming an astronomer; but soon the chemical side absorbed his attention, and during the remainder of his life his time was divided between pure chemistry

and chemical mineralogy, although he always took especial pleasure in the examination of crystalline forms. Somewhat later, he was advised by Pasteur to seek an entrance to the Academy of Science in the section of mineralogy, to which Pasteur himself belonged, but Friedel preferred to make chemistry his principal study.

On November 10th, 1854, Friedel entered Wurtz's laboratory, and soon became its most distinguished pupil. There were some sixteen places, of which usually one-third were occupied by foreigners, particularly Russians, Germans, Austrians, and Italians. The rooms at the School of Medicine were inconvenient, having been designed for other purposes, and the balances were placed in an anatomical lecture room; yet this school succeeded in some measure to that of Liebig, and was visited by chemists of all nations; for European science still held to the traditions of the time of Humboldt, and a sojourn, however short, at Paris was considered a desirable part of a scientific education.

Friedel's researches upon acetones and aldehydes were made at this time, 1857—1863, in the laboratory of the School of Medicine, and his views of their constitution, and his discovery of secondary propylic alcohol, were immediately recognised as important contributions to chemical science.

In 1866, the privilege of a small laboratory at the School of Mines was attached to the place of Curator of the mineralogical collection, and it was there that Friedel's work in mineralogy was done, as well as the researches upon silicon compounds and the aluminium chloride reaction. He had, between 1866 and 1880, an apartment in the buildings of the School of Mines. In 1869, he took his Doctorate degree, offering two theses, one upon acetones and aldehydes, and the other upon the pyroelectric properties of crystals. In 1871, he gave the lectures in mineralogy at the Normal School (*Ecole normale supérieure*), replacing Des Cloizeaux.

In 1876, he was appointed Professor of Mineralogy at the Sorbonne, succeeding Delafosse, and he there organised a laboratory for mineralogy. Two years later, he was chosen Member of the Academy of Science in the chemical section, filling the place left vacant by the death of Regnault.

The death of Wurtz in 1884 left Friedel the oldest representative of Wurtz's school and he succeeded to Wurtz's professorship of organic chemistry at the Sorbonne, exchanging this chair for that of mineralogy. The laboratory accommodation for chemical students was very insufficient at Paris and the old buildings at the Sorbonne were still more unsuited to such work than were those of the School of Medicine. A project for new and greatly enlarged buildings was under consideration, but with small prospect of immediate realisation, so that Friedel devoted his energy to the construction of a temporary

laboratory building beyond the Luxembourg Garden in the Rue Michelet, where also the inorganic laboratories of the Sorbonne under Troost were located. These rooms, although lacking the luxury of the modern laboratory, proved to be convenient and the places for about fourteen students were always filled.

In January, 1895, the new laboratories at the Sorbonne, built upon Friedel's plans, were opened with places for thirty students in organic chemistry, and at the same time he organised a three years' course of lectures and laboratory instruction in industrial chemistry at the provisional laboratories in the Rue Michelet. Such instruction had heretofore been wanting in Paris. It was undertaken at Friedel's instigation by the Municipal Government, and the attention required by the initial steps, and afterwards by the direction of this new course, formed an important occupation during the last four years of his life.

He took the chief part in 1899 in founding the *Revue Générale de Chemie pure et appliquée*, which is largely devoted to industrial applications. Friedel was associated with Wurtz in editing the *Dictionnaire de Chemie pure et appliquée* and after Wurtz's death in 1884 became the chief editor of the supplements, of which the second has only progressed to the letter G. During the later years of his life, editorial work, together with the work upon committees and administrative duties, engrossed more and more of his time, and he often regretfully looked back upon the hours spent upon experiments in his laboratory which he ever considered the most enjoyable.

He was one of the founders of the French Chemical Society, four times its President, and a constant attendant at its sittings. He took the initiative in founding the French Society for the advancement of Science in 1885, and presided at the meeting at Nancy in 1886. He presided at the International Congress of Chemists held in 1892 at Geneva for the reform of the nomenclature of the fatty acid series, and up to the time of his death was occupied with the arrangement of a similar meeting to attempt the construction of a common system of nomenclature for the other classes of organic compounds.

He was awarded the Davy medal by the Royal Society in 1880; received the degree D.C.L. from Oxford University in 1894.

The following societies conferred their membership or honorary membership on Friedel: Foreign member of the English Chemical Society, 1876; Industrial Society of Mulhouse, 1879; Physical Society of Geneva, 1880; Royal Society of Turin, 1882; Academy dei Lincei, 1883; Academy of Munich, 1883; Royal Academy of Lisbon, 1890; Natural History Society of Maxon, Society Antonio Alzato Mendio, 1890; Roy Society of Brussels, 1892; Society of Physics and Chemistry of Bucharest, 1892; Literary and Philosophical

Society of Manchester, 1892; honorary member of the German Chemical Society, 1894; Royal Society of Sweden, 1894; corresponding member of the British Association for the Advancement of Science, 1895; Royal Society of St. Petersburg, 1895; Physical Society of Frankfort, 1898.

He was made Chevalier of the Legion of Honour in 1869, and Officer in 1886. He was Officer of Public Instruction, and was also Commander of the Orders of St. James of Portugal and of the Crown of Roumania.

Before taking up the record of Friedel's work in science, a further description may be given of the fortunate surroundings, which not only favoured the development of a judicious and amiable character, but also gave full play to his scientific ability. His tastes found immediate and hearty appreciation and support from his parents and relations, and sufficient pecuniary resources were always at his command to allow him to do his chosen work in the best way.

His love of science was hereditary. His father, Charles Friedel, although beginning his long commercial career in a banker's office at the age of thirteen, attended scientific lectures at Strasbourg whenever he had the opportunity, and, at the age of eighty-four, expressed his regret that necessity had prevented him from following a scientific career, and his satisfaction that the choice had been offered to his son.

The mother was a woman of strong character, and came of a professorial family. Her father was George Louis Duvernoy, a physician established at Mountbéliard, and later Dean of the Strasbourg Faculty of Science, and finally Professor at the Museum of Natural History at Paris.

The gathering of a small collection of minerals by the boy was encouraged, a laboratory was tolerated in his father's house, and later, when he was staying with his grandfather Duvernoy, he was aided in his choice of studies by the veteran in science, until failing health made the older man dependant upon the younger. A letter written in 1854 describes occupations which are not generally attributed to a student in the gay capital; thus the day was devoted to arduous studies to prepare for the baccalaureate examination, long evenings were spent in watching with or reading to the grandfather, and on Sundays some hours were given to visiting the poor.

Senarmont, with whom he began mineralogical work, took a strong and friendly interest in the young student, and Friedel's friendship with Wurtz was a very important factor in his career. Both Alsacians, united by tastes, opinions, and pursuits, the elder chemist opened the way for the younger in professional and editorial work. Wurtz's high reputation, his activity in public affairs as well as in science, led to the creation of the chair of organic chemistry at the

Sorbonne, and after Wurtz's death in middle age, Friedel's studies and talents naturally marked him out as the successor. Wurtz's influence in Government circles also prevailed, after long-continued effort, in obtaining support for laboratory instruction, and, shortly before his death, the orders were given for the construction of a large modern laboratory at the Sorbonne, the plans of which were matured, and the construction superintended, by Friedel.

The two friends were very intimate, and were thoroughly in accord regarding all matters of public and scientific interest, but in later years Wurtz became much occupied with duties connected with his senatorship, whilst Friedel was never diverted from scientific pursuits. In consequence, the share of the latter in editing Wurtz's chemical dictionary became larger.

Until within a few years of his death, Friedel never had a well-equipped laboratory provided with labour-saving contrivances, nor was he disposed to have much work done by assistants, preferring to leave very ample opportunities to all those about him for doing original work and publishing it alone, whilst aiding them untiringly with his counsels. For these reasons, the volume of his contributions to chemical research is not very large, and many an idea passed into other hands for execution.

Most of the work in organic chemistry was done in a small room in the fine palace on the Luxembourg Gardens which is used for the School of Mines, whilst a dark, vaulted cellar served for the artificial production of minerals at high temperatures and pressures. Here Friedel and Edmond Sarasin heated "Jacob" to a very low red heat at whatever pressure boiling water gives at that temperature. The origin of the name is lost, but "Jacob" was the only designation of a very heavy steel tube lined with platinum, in which water and pure materials intended to make silicates were heated overnight, and the fate of "Jacob" was a matter of lively interest each morning in the laboratory. There was no serious explosion, but any attempt to economise in the weight of the thick interior platinum tube led to a disaster.

Friedel married Miss Emilie Koechlin of Mulhouse on December 29th, 1856. One son and four daughters were born of this marriage. The surrender of Paris in 1871 brought to him the sad news of the death of his charming and amiable wife, who had been obliged by failing health to pass the winter at Montreux and died on January 19th, 1871, while her husband was serving in the national guard during the siege. On April 7th, 1873, he married Miss Louise Combes, daughter of the director of the School of Mines, and a son was born of the second marriage. The character and education of his wife, who still survives, made her a most efficient aid and companion. During his last illness,

his wife and several of his children were with him at the house of his son-in-law, Professor Henri Bois at Montauban.

Friedel's life in Paris was wholly devoted to science, and was not unlike that of the professor in a university town. Weekly evening receptions kept him in touch with his scientific friends and scholars. In the discussions which took place on these occasions, his modesty led him instinctively to play the part of a listener until every one had expressed an opinion, and then all were glad to hear a new and fundamental treatment of the subject from Friedel's lips. It is a piece of good fortune for an honest man to have a face expressive of character, and his was eminently one which immediately convinced a new acquaintance that the man was incapable of guile, and thus inspired ready confidence and the ease of intercourse which goes with it.

He was a lover of music and of art, and his favourite recreation was sketching from nature. He took a strong and judicious interest in political affairs. Very happy in his family life, and in many intimate friendships, escaping unfriendly rivalries by his character and circumstances, he was permitted from the beginning to the end to carry on with a single mind the pursuits which he loved. The pursuit of science and his duties as a husband, father, friend, and citizen made up Friedel's existence. He was always disposed to work somewhat beyond his strength, and in 1885 a severe illness diminished considerably for the remaining years his capacity for experimental work, but not for editorial labours.

One of the elements contributing to a certain retirement from the disturbing interests of life in the French capital were the associations into which Friedel's Protestant faith (*Eglise réformée*) led him. Isolation is too strong a word to be applied to Protestant society at Paris, and yet in certain ways their habits of thought are different from those of their neighbours. Strong motives for these differences still survive among the Protestants of the older generation from the south of France, and the second wife of Friedel cannot forget having passed her childhood near Nîmes in a house where the coffins of her relations occupied one of the drawing rooms because, as Protestants, they were refused Christian burial. No memories of persecutions haunt the immediate past of the Alsatian Protestants. Those who elected French nationality after the war, or who, like Friedel, were fortunate in having already chosen their residence in Paris, have had full recognition of their patriotism and of their value as citizens; nevertheless, a mental barrier is raised to some extent between Protestants and Catholics, and curious testimony of this attitude was lately offered when the latter joined with an army of Freethinkers and affected to confound the Protestants with the Jews. Not religious controversies, but different habits of thought, as marked as racial characteristics,

make a distinct, although faint, line of separation between general Parisian society and that in which Friedel moved. For a man of his character, it must not be supposed, however, that any distinct obstacle prevented perfect freedom of intercourse with men of all shades of opinion.

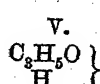
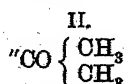
After very deliberate reflection, the writer cannot forbear adding a piece of personal testimony to this sketch of a life's work. During thirty-eight years in which a close friendship made him a witness of conduct and actions, he cannot recall a single instance in which he would have wished his friend to have thought or acted otherwise than he did.

### *Chemical Researches.*

Friedel at the age of twenty-five chose the ketones (acetones they were called at that time) for the subject of his first research, and he was fortunate enough to establish experimentally the properties of the first of the important series of secondary alcohols, besides preparing many new ketones and their derivatives (*Ann. Chim. Phys.*, 1869, [iv], 16, 310). While preparing new substances, he held the theoretical side of the subject distinctly in view, and did much to set it on a firm basis.

At this period, Gerhardt was the authority on organic chemistry. The type theory had been well developed, and owed much of its value to the discoveries of the compound ammonias and the bivalent alcohols by Wurtz. Kekulé, in the first volume of his organic chemistry, published in 1861, used the existing ideas of types and radicles in a much more rational way than his contemporaries, but there was some confusion in the use of what he called rational and reactional formulæ, and much remained to be done in presenting schemes of structure capable of explaining the relation between the constitution and properties of a substance. With greater or less distinctness, the chemists of the day recognised the possibility of explaining functions by formulæ, and Friedel was the first to so enlarge the data as to give what were accepted as convincing proofs of the dependence of the functions of the CO group in acetones upon the form of combination.

Kekulé devotes only seven pages in his first volume to the known ketones; he does not mention them under the section "Carbonyl compounds," and he uses five formulæ for acetone:



The first two he calls rational formulæ, and probably considered II to be a developed form of I and V of IV. On page 617, he says that



the mesityl compounds point to V as the rational formula for acetone; the remaining reactions are explained by III.

It is unnecessary to give a catalogue of the new ketones obtained by Friedel, using known methods. In his first paper (*Compt. rend.*, 1857, 45, 1013), he describes phenyl methyl ketone and methyl butyl ketone. He also studied the products of the action of phosphorus pentachloride on the ketones, obtaining a new propylene dichloride and monochlorinated propylene. The chief purpose of this work was to furnish further proofs of a similarity of function between aldehydes and ketones. This had already been indicated by certain reactions common to both series. Thus Limpricht had described the additive compounds with sodium hydrogen sulphite, and Städeler those with hydrocyanic acid. Cahours had shown that an aldehyde treated with phosphorus pentachloride does not break up like an alcohol or an ether, but that two atoms of chlorine are substituted for oxygen. Friedel completed the demonstration by showing that acetone behaved in the same way.

Friedel, in a second paper (*Compt. rend.*, 1862, 55, 53), described the behaviour of aldehydes and ketones on reduction with sodium amalgam (zinc and an acid cannot be employed because the production of hydrogen is arrested by aldehydes). Wurtz had used the sodium reduction for ethylene oxide, but was prevented from applying it to aldehydes because of the resinifying action of caustic soda on common aldehyde. Friedel succeeded in reducing benzaldehyde and valeraldehyde to the corresponding alcohols, and acetone to a propylic alcohol, which was not identical with the primary one (b. p.  $97.3^{\circ}$ ) discovered by Chancel in 1853 among fermentation products. He believed it to be identical with a propylic alcohol prepared by Berthelot in 1855 by the action of sulphuric acid on propylene.

No experiments had been made to prove that Chancel's alcohol gave propionic acid and Berthelot's alcohol acetone on oxidation, and Friedel considered it superfluous to ascertain whether a substance derived from acetone by reduction would give acetone on oxidation. Kolbe took advantage of this omission to bring forward his theoretical views, predicting this nearly evident fact, and at the same time giving a clear exposition of the difference between a primary and a secondary alcohol. The capital point was the discovery of the relation of a secondary alcohol to its oxidation product, and it may be considered that Friedel's reduction of acetone accomplished this task.

Berthelot (*Ann. Chim. Phys.*, 1855, [iii], 43, 399) afterwards tested the alcohol derived from propylene, and found that it also gave acetone on oxidation.

It should be stated that Kolbe recognised more clearly than the other chemists of that time the significance and the importance of the

existence of two kinds of propylic alcohol, one of them offering the first example of a secondary alcohol.

Friedel also observed the formation of pinacone, and pointed out its true constitution. It had been discovered by Fittig, and supposed to be a hydrate of  $C_6H_{12}O$ . Later, in 1873, Friedel and Silva (*Bull. Soc. Chim.*, [ii], 19, 289) described a process for the convenient preparation of large quantities of pinacone.

*The True Formula of Lactic Acid.*—Wurtz and Friedel (*Ann. Chim. Phys.*, 1861, [iii], 63, 101) showed the difference between the alcoholic and the acid functions of the two hydroxyl radicles in lactic acid, and the corresponding properties of the two esters. They explained that lactic acid is intermediate between propyl glycol and malonic acid, as glycollic acid is intermediate between glycol and oxalic acid. The alcoholic hydroxyl they call basic.

Friedel and Machuca (*Compt. rend.*, 1861, 52, 1087) described the synthesis of lactic acid from bromopropionic acid, glyceric acid from dibromopropionic acid, hydroxybutyric acid from bromobutyric acid, and butalanine by the action of ammonia on bromobutyric acid.

*The Theory of Double Decompositions.*—Friedel and Crafts (*Compt. rend.*, 1863, 57, 877, 986) showed that when the ester of an alcohol is heated with another alcohol, one radicle partially displaces the other as one metal displaces another in salts. Mixed esters of polybasic acids are formed by a similar process. Alkyl iodides heated with esters give rise to similar displacements, but here a little hydrogen iodide is set free, and serves to esterify a large quantity of alcohol.

Friedel subsequently made a contribution to the theory of esterification by means of halogen acids by showing that, in presence of phosphoric oxide, hydrogen chloride converts a considerable proportion of benzoic acid into benzoyl chloride, and supposes that a similar transformation contributes to esterification (*Compt. rend.*, 1869, 68, 1547).

The experimental difficulties of these early problems were not great, and chemists were rewarded for their labours by the rapid appearance of new substances; the next research led on to more difficult ground.

*Silicon Compounds.*—Friedel's interest in mineralogy led him to take up the important question of the atomic value of silicon. The school of Wurtz had completely accepted the authority of Avogadro's law under which  $SiCl_4$  represents the molecule of the best known volatile compound of silicon; but Buff and Wöhler discovered in 1857 a compound,  $Si_2Cl_6 \cdot 2HCl$  ( $Si = 21$ ), whose formula is incompatible with the quadrivalence of silicon. They described the new substance as a solid boiling at  $42^\circ$ , obtained by the action of hydrogen chloride on silicon. This support for the old trivalent formula was welcomed by chemists who had been accustomed to the calculations of mineral analysis established by Berzelius. The new discovery, however, did

not convince Friedel, who considered that, beside the vapour density of silicon tetrachloride, the work of Marignac and the whole assemblage of facts pointed to the tetratomicity of silicon, and sought a confirmation of his views in the organic compounds of the element.

Friedel and Crafts (*Compt. rend.*, 1863, 56, 324; 57, 319) took up the work of Ebelmen (*Annalen*, 1844, 52, 324; 1846, 57, 319), expecting to find that the normal ester  $\text{Si}(\text{OEt})_4$  would form a series of condensed esters of which the simplest, upon a quadrivalent scheme, must be  $\text{Si}(\text{OEt})_3 \cdot \text{O} \cdot \text{Si}(\text{OEt})_3$ . It was proved that this compound, and others more complicated, for example,  $\text{Si}(\text{OEt})_3 \cdot \text{O} \cdot \text{Si}(\text{OEt})_2 \cdot \text{O} \cdot \text{Si}(\text{OEt})_3$ , were produced by the action of a trace of water on the normal ester. The first of the series can be easily purified by fractional distillation; but the boiling points of the other members, even in a vacuum, are so high that a separation becomes impossible, since they boil at temperatures at which glass softens, without giving off much gas, but undergoing polymeric transformations. The quadrivalent character of silicon was also shown by allowing anhydrous alcohol to act on an excess of silicon tetrachloride, when a series of well defined chlorohydrins was obtained with the formulæ  $\text{SiCl}(\text{OEt})_3$ ,  $\text{SiCl}_2(\text{OEt})_2$ ,  $\text{SiCl}_3\text{OEt}$ . The composition and vapour densities of these substances agree only with the atomic weight 28 for silicon.

The polysilicic esters recall the series of polyglycols and the analogy between the quadrivalent elements, silicon and carbon, was so marked in all these organic compounds, that it seemed desirable to attempt to replace carbon by silicon in a hydrocarbon and to endeavour to make silicononane  $\text{SiC}_8\text{H}_{20}$ . It was thought that this domain might belong to Professor Frankland, but after consulting him Friedel and Crafts were courteously informed that the research was open to them, Professor Frankland stating that the few attempts which he had made to obtain a reaction between silicon chloride and zinc ethide had not been successful. A rather high temperature is required and some gas is produced, but large quantities of a pure substance,  $\text{Si}(\text{Et})_4$ , distilling at  $153^\circ$  were prepared. Unlike most organo-metallic compounds, this substance is very stable towards all reagents, and has completely the aspect of a hydrocarbon except that when it burns, it forms a smoke of silica. In it, chlorine can be substituted for hydrogen and then hydroxyl for chlorine, giving silicononylic alcohol,  $\text{SiC}_8\text{H}_{19} \cdot \text{OH}$ . In the same way that petroleum hydrocarbons are accompanied by small quantities of oxidation products, mostly ketones and alcohols, so also silicon tetrathide, both during its formation and afterward by contact with air, is liable to an oxidation more rapid than petroleum, but still very slow. On account of oxidation, some difficulty was experienced in obtaining the silico-hydrocarbon pure until the oxygenated products were separated.

by solution in concentrated sulphuric acid, which does not attack the hydrocarbon. Thus an unmistakable analogy is established between the general character of carbon and silicon compounds, and Friedel afterwards made use of this resemblance in building up rational formulæ for mineral silicates.

Silicic esters of other alcohols were prepared and also silicon tetraethide, but with much more difficulty than the ethide.

It may be noticed that when the esters are slowly decomposed by penetration of moisture during many years, an opaline silica, hard enough to scratch glass, is obtained.

Friedel and Ladenburg (*Bull. Soc. Chim.*, 1867, [ii], 7, 322) took up the study of Buff and Wöhler's silicon hydrochloride,  $\text{Si}_2\text{Cl}_3\cdot 2\text{HCl}$  ( $\text{Si}=21$ ), and showed that it could be separated by fractional distillation into silicochloroform,  $\text{SiHCl}_3$ , boiling at  $36^\circ$ , and silicon tetrachloride,  $\text{SiCl}_4$ , boiling at  $55-60^\circ$ . By action of alcohol, the former gives  $\text{SiH}(\text{OEt})_3$ , and with water an oxide,  $\text{Si}_2\text{H}_2\text{O}_3$ , which corresponds with formic anhydride containing silicon instead of carbon.

An impure silicon hydride was described by Buff and Wöhler; the pure compound was prepared by the action of sodium upon the ether  $\text{SiH}(\text{OEt})_3$ .

Friedel and Ladenburg (*Annalen*, 1868, 145, 174) found that a sulphide to which Pierre gave the formula  $\text{SiCl}_2\text{S}$  ( $\text{Si}=21$ ) really contained hydrogen and was a silico-trichloromercaptan,  $\text{SiCl}_3\text{SH}$ . The SH radicle can be replaced by bromine to obtain  $\text{SiCl}_3\text{Br}$ .

Friedel and Ladenburg (*Compt. rend.*, 1868, 66, 530) obtained  $\text{SiCl}_3\cdot\text{O}\cdot\text{SiCl}_3$  by passing silicon tetrachloride through a red hot porcelain tube, the oxygen being taken from the porcelain. This oxychloride gives with alcohol the same ester,  $\text{Si}(\text{OEt})_3\cdot\text{O}\cdot\text{Si}(\text{OEt})_3$ , as that obtained by the action of water on the ortho-ester  $\text{Si}(\text{OEt})_4$ . With zinc ethide, it gives  $\text{SiEt}_3\cdot\text{O}\cdot\text{SiEt}_3$  and this oxygenated compound seems also to be formed in the preparation of silicon ethide.

Silicon tetriodide,  $\text{SiI}_4$ , and silico-iodoform,  $\text{SiHI}_3$ , were prepared by the action of iodine and hydrogen iodide on heated silicon, and Buff and Wöhler's formula,  $\text{Si}_2\text{I}_3\cdot 2\text{HI}$ , for the product of the reaction, was shown to be erroneous (Friedel, *Bull. Soc. Chim.*, 1868, [ii], 9, 1). The compound,  $\text{SiBr}_3\text{I}$ , boiling at  $200^\circ$  was obtained by the action of bromine on silicon tetriodide,  $\text{SiI}_4$ .

Silicon triiodide,  $\text{Si}_2\text{I}_6$ , was obtained by heating the tetriodide,  $\text{SiI}_4$ , with finely divided silver at  $300^\circ$  (Friedel and Ladenburg, *Compt. rend.*, 1869, 68, 920); a non-volatile substance,  $\text{SiI}_2$ , was also obtained which yields hydrogen on treatment with potassium hydroxide. The triiodide reacts with water to give the compound  $\text{Si}_2\text{O}_2(\text{OH})_2$ , which may be regarded as oxalic acid, in which carbon is replaced by silicon.

From the triiodide, the trichloride,  $\text{Si}_2\text{Cl}_6$ , boiling at  $146^\circ$ , was ob-

tained by treatment with mercuric chloride (Friedel, *Ber.*, 1869, 2, 747), and the ethide,  $\text{Si}_2(\text{C}_2\text{H}_5)_6$ , by the action of zinc ethide.

Silicopropionic acid,  $\text{C}_2\text{H}_5\text{Si}\cdot\text{O}\cdot\text{OH}$ , was prepared by the action of zinc ethide on the chlorohydrin,  $\text{SiCl}(\text{OC}_2\text{H}_5)_3$ , and subsequent saponification of the product.

This brilliant investigation by Friedel and Ladenburg, in which frequently great experimental difficulties were overcome, established with unhopd-for completeness the strong analogy between silicon and carbon compounds.

*Titanium Compounds.*—Friedel and Guérin (*Compt. rend.*, 1875, 81, 889), by the action of silver, reduced titanium tetrachloride,  $\text{TiCl}_4$ , to the trichloride  $\text{Ti}_2\text{Cl}_6$ , but found that when an attempt is made to purify the latter by distillation, it breaks up into the dichloride,  $\text{Ti}_2\text{Cl}_4$ , and tetrachloride,  $\text{TiCl}_4$ . By interaction with bromine, the dichloride gives the compound  $\text{TiCl}_2\text{Br}_2$ . Bromine converts the trichloride,  $\text{Ti}_2\text{Cl}_6$ , into the compound  $\text{TiCl}_3\text{Br}$ ; the oxychloride,  $\text{TiOCl}_2$ , was also prepared.

In the description of Friedel's mineralogical work will be found an account of titanic oxides derived from these chlorides.

Friedel and Guérin (*Ann. Chim. Phys.*, 1876, [v], 8, 24) also studied the compounds of titanium with nitrogen, and isolated the nitrides,  $\text{Ti}_2\text{N}_2$  and  $\text{Ti}_3\text{N}_4$ .

*Mixed Halogen Compounds of Hydrocarbons.*—Friedel and Silva (*Jahresb.*, 1870, 419; *Compt. rend.*, 1871, 73, 955; *Bull. Soc. Chim.*, 1872, [ii], 17, 537) found that only one-half the bromine in bromopropylene is replaced by chlorine when treated with mercuric chloride; with ethylene chlorine, the action is complete at  $180^\circ$ , and all the chlorine is replaced. They obtained 1:2-dichloropropylene, 1:3-dichloropropylene, and 2:3-dichloropropylene by new modes of synthesis. The physical constants and chemical reactions of these bodies were determined, and so far as the methods of the day permitted, their rational formulæ were fixed.

The action of iodine monochloride on chloroform was found to give rise to carbon tetrachloride,  $\text{CCl}_4$  (Friedel and Silva, *Bull. Soc. Chim.*, 1872, [ii], 17, 537); with ethylene or propylene, iodine monochloride formed dichlorides with separation of iodine.

*Synthesis of Glycerol.*—Friedel and Silva (*Compt. rend.*, 1871, 73, 1379; 1872, 74, 805) undertook the synthesis of glycerol from the elementary components. At this time, although it was recognised that the rapidly increasing number of such syntheses held out a prospect for making all natural products artificially, yet few means were at hand for supplanting the work of nature, and the synthesis of glycerol had not been accomplished. So soon as the true formula was known,  $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , the only

difficulty lay in attaching a halogen atom to each of the three carbon atoms. At first, allyl iodide was used for the preparation of trichlorohydrin, but afterwards, in answer to an objection from Berthelot that allyl derivatives came from glycerol, propylene was prepared from acetone, and by treating this with chlorine and with iodine monochloride, trichlorohydrin was obtained, which was easily transformed into glycerol.

*Dimethyldiethylmethane* was one of the most important substances prepared during an extended study of the products of the action of the halogens on the simpler hydrocarbons. It was the first example of the type  $CR_4$ , and was prepared by the action of zinc ethide on dimethylmethylenedichloride,  $(CH_3)_2CCl_2$  (Friedel and Ladenburg, *Compt. rend.*, 1866, 63, 1083).

A new mode of preparing allylene was discovered in the action of caustic potash on dimethylethylene chloride,  $CCl_2(CH_3)_2$  (Friedel, *Compt. rend.*, 1864, 59, 294), and of phenylacetylene in the action of caustic potash on the compound  $C_6H_5 \cdot CCl_2 \cdot CH_3$  (Friedel, *Compt. rend.*, 1868, 67, 1192).

*Dimethyl Ether Hydrochloride*.—At a time when it was imperfectly recognised that the variations from the law of Avogadro were due to dissociation, Friedel discovered a compound whose dissociation was complete at a very low temperature: namely, the combination of methyl ether and hydrogen chloride,  $6C_2H_6O, 5HCl$ , a liquid boiling at  $-2^\circ$ . Friedel studied the dissociation tension of this substance at various temperatures, and concluded it was a true chemical compound, although highly dissociated in the gaseous state (*Compt. rend.*, 1875, 81, 152, 236).

*The Aluminium Chloride Reaction*.\*—The experiments which demonstrated the wide scope of the reaction were so easy of execution that those described in the first three papers were carried out in the course of five or six weeks. The discovery sprang from an accidental observation of the action of metallic aluminium on chloride of amyl. It was soon seen that the metallic halogen salt and not the metal was the active body, and a similar fact was found to give the true explanation.

\* The first publications were made in 1877 (*Compt. rend.*, 84, 1392, 1450; 85, 74). A complete account of work done up to 1887 is given in the *Annales de Chimie et Physique*, 1884, [vi], 1, 449; 1887, 10, 411; 11, 263; and 1888, 14, 433). A good presentation of the literature of the aluminium chloride reaction is to be found in Elbs' *Synthetische Darstellungs Methoden* (vol. ii, pp. 140—171). He says that the Friedel-Crafts reaction is among all synthetical methods the one most commonly used, and cites a nearly complete list of its employment by its discoverers and its extension by other chemists. A curiosity in chemical literature is the book by Seelig upon organic reactions which makes 23 citations of 20 authors on the aluminium chloride reaction without mention among them of the name of Friedel.

ation of the excellent synthetical method discovered by Zincke (*Ber.*, 1873, 6, 137), in which zinc dust and benzyl chloride were used to obtain diphenylmethane. So sensitive is the reaction in some cases that benzyl chloride is decomposed by long distillation in a copper vessel if brass solder has been used, zinc chloride taken from the solder being the condensing agent.

The results obtained in the very beginning seemed to show that any number of halogen atoms in a paraffin could be replaced by phenyl; that the six hydrogen atoms in the benzene ring could each, with equal ease, be replaced successively by alkyls; and that a halogen in an aromatic side chain acted with even more readiness on the benzene ring. Halogens substituted in the aromatic ring were inactive in presence of aluminium chloride even at high temperatures. Some few exceptions were found later to these generalisations. All these reactions between chlorinated compounds and aromatic hydrocarbons took place at the ordinary temperature, or with slight warming in presence of aluminium chloride, bromide, or iodide. Zinc or ferric chloride had a similar effect, but in a less degree. Chlorides of magnesium, cobalt, copper, mercury, and antimony are without effect.

The chlorides of mono- or di-basic acids react with benzene and its homologues, giving ketones. The presence of alcohol or acids, that is, of hydroxy-compounds, prevents the aluminium chloride reaction, and it also could not at first be carried out with ethers. New compounds were obtained, like phthaloketone and pentamethylbenzene, and the way was immediately opened for preparing with great ease numerous homologues of benzene and new ketones. The preparation of such hydrocarbons as durene and hexamethylbenzene was made easy, and consequently mellitic acid could readily be obtained by a process of oxidation. Also, triphenylmethane and its homologues were prepared on a large scale, and these seemed to offer a new method of making aniline dye stuffs commercially. Unfortunately, the discoverers had at that time only a very small laboratory, with no place for students, and not even provided with the convenience of running water, whilst circumstances separated them for a time and retarded the progress of the work in clearly indicated directions.

The first publication in 1877, beside containing a record of the facts above stated, offered a theory of the reaction based upon analogies with the properties of organo-metallic bodies. It was supposed that all the observed effects might be explained by the existence, even in small proportion, of an organo-metallic chloride,  $C_6H_5 \cdot Al_2Cl_5$ , which, being constantly decomposed according to the equation  $C_6H_5 \cdot Al_2Cl_5 + RCl = C_6H_5R + Al_2Cl_5$ , and constantly renewed, would explain the contact action of aluminium chloride. This theory was kept in view

throughout subsequent work, and was strengthened by many new facts, and particularly by those relating to the readiness with which oxygen, sulphur, carbon and sulphur dioxides, and cyanogen are absorbed by the benzene compound with aluminium chloride, giving respectively phenol, phenylmercaptan and phenyl sulphides, benzoic acid, phenylsulphonic acid, and benzonitrile. The small quantity of each of these products obtained may be ascribed to the insolubility of the gases in benzene.

The action of the compound  $C_6H_5AlCl_2$  should be analogous to that of aluminium triphenyl,  $(C_6H_5)_3Al$ . The latter was prepared by the action of aluminium on mercury diphenyl, and gives, with benzyl chloride, diphenylmethane; with oxygen, phenol; and with sulphur, phenylmercaptan, but has no action on halogens substituted in the benzene ring. Hence a well-known organo-metallic compound gives the same reactions as aluminium chloride and benzene.

Zinc ethide is known to break up by heating into ethylene and ethane. Here, again, the analogy holds good, for hydrocarbons heated with aluminium chloride break up into simpler saturated compounds which are easily isolated, and into complex non-saturated ones. The latter are probably derived from simple unsaturated substances,  $C_nH_{2n}$  or  $C_nH_{2n-2}$ , &c., which undergo condensation in presence of aluminium chloride, a reaction which can be observed in the simplest stage between benzene and ethylene,  $C_6H_6 + C_2H_4 = C_6H_5 \cdot C_2H_5$ . The condensation proceeds much further when halogen derivatives of the paraffins are treated with aluminium chloride, undistillable products very poor in hydrogen being formed, together with volatile paraffins.

The last investigation of Friedel in this field concerned the action of aluminium chloride on one of the simplest of the paraffins, and, in conjunction with Gorgeu (*Compt. rend.*, 1898, 127, 590), it was found that normal hexane treated with aluminium chloride at  $35^\circ$  gives pentane and butane together with condensed products.

The aromatic hydrocarbons are usually more stable, but they are all decomposed by heating with aluminium chloride at high temperatures. Naphthalene is very easily attacked, giving benzene and an excellent yield of hydrides of naphthalene. Triphenylmethane is also easily decomposed, giving diphenylmethane, toluene, and benzene. Benzene gives diphenyl and other products.

The alkyl groups in aromatic compounds are subject to migrations giving rise to higher and lower homologues. These changes and isomeric transformations of chloro-paraffins were found to limit the possibilities of the reaction.

The action of aluminium chloride on substances associated with petroleum, and the elimination of sulphur from them, was studied.



In consequence of the claims of various authors to have discovered the destructive action of aluminium chloride, a restatement was made of the original facts with some additions (Friedel and Crafts, *Trans.*, 1882, 41, 115; *Compt. rend.*, 1885, 100, 692).

Exceptions to the general rules were discovered later. In some cases, ortho-dihalogen substitution products in the benzene ring are attacked. In  $\text{CH}_2\text{Cl}\cdot\text{COCl}$ , only the chlorine in the carbonyl group is active, and in the case of carbon tetrachloride only three atoms of chlorine are replaced by phenyl, and diphenyl is formed as a bye-product, as was shown by Fischer. The mistake in the first paper, which announced the formation of tetraphenylmethane, was due to an error in Watt's Dictionary, 2nd Suppl., p. 948, which gives  $335^\circ$  for the boiling point of triphenylmethane. The product isolated boiled  $24^\circ$  higher, namely, at  $359^\circ$ , and was therefore assumed to be a tetraphenyl compound, the percentage composition of the two compounds being not far different. Subsequent determinations made by Crafts with a hydrogen thermometer showed  $359^\circ$  to be the boiling point of pure triphenylmethane.

The synthesis of triphenylmethyl was studied anew in 1882 (*Bull. Soc. Chim.*, [ii], 37, 6), and the conditions for obtaining a good yield were described. The proportion of diphenylmethane produced as bye-product is only about one-fourth that of the triphenylmethane. Triphenylcarbinol was obtained from the product of the interaction of carbon tetrachloride and benzene by treatment with water.

These are the principal facts which characterise the reaction, and which have a bearing upon its theoretical explanation; it is only necessary to cite a few examples of its use in preparing pure products.

A class of ortho-ketonic acids is easily obtained by means of the anhydrides, such as phthalic anhydride,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}\cdot\text{OH} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}$ .

Phthalic chloride,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CCl}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$ , treated with aluminium chloride and benzene, gives phthaloketone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_5)_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$ . It was hoped to effect the synthesis of anthraquinone by this reaction, but the yield is very poor. It suffices, however, to indicate the existence of a symmetrical phthalic chloride which gives the reaction  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COCl} \\ \diagup \quad \diagdown \\ \text{COCl} \end{smallmatrix} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4 + 2\text{HCl}$ .

Anthracene and its homologues can be obtained by a reaction which takes place according to the equation  $3\text{CH}_2\text{Cl}_2 + 3\text{C}_6\text{H}_6 = \text{C}_2\text{H}_2(\text{C}_6\text{H}_5)_2 + \text{C}_6\text{H}_5\cdot\text{CH}_3$ . The principal product, however, is diphenylmethane.

When toluene is substituted for benzene, dimethylantracene is formed.

The fundamental synthesis of a ketone by the action of carbonyl chloride on benzene in presence of aluminium chloride takes place with such regularity that when pure crystallised benzene is used, the crude product boils within a limit of  $0.2^{\circ}$ , and forms the best substance for standardising thermometers near  $306^{\circ}$ .

*Vapour Density Determinations.*—The molecular weight of aluminium chloride was found by Nilson and Pettersson to approach that required by the formula  $AlCl_3$ , and consequently to accord with the trivalent place usually assigned to aluminium in the periodic arrangement of the elements (*Zeit. physikal. Chem.*, 1887, 1, 459).

Friedel and Crafts (*Compt. rend.*, 1888, 106, 1764; 107, 306) drew attention to the fact that the experiments of Nilson and Pettersson began at  $440^{\circ}$ , and that the method of Victor Meyer, which was used, is unsuitable for determinations near the boiling point of the substance. The physical properties of aluminium chloride were studied, and a careful series of determinations of the boiling point of aluminium chloride between the pressures of 252 and 2277 mm. of mercury were made. The chloride was liquefied under pressure, and crystallised in beautiful, white, transparent crystals melting at  $186.5^{\circ}$ , or a little above the boiling point under atmospheric pressure, namely,  $183^{\circ}$ .

Vapour density determinations by Dumas' method, modified to obtain different tensions, were made between  $218^{\circ}$  and  $432^{\circ}$ , and the vapour density was found to correspond with that required by the molecular formula  $Al_2Cl_6$ .

Under similar conditions, vapour densities corresponding to the formulæ  $Fe_2Cl_6$  and  $Ga_2Cl_6$ , were found for ferric and gallium chlorides.

*Camphoric Acid.*—Friedel (*Compt. rend.*, 1891, 113, 825; *Bull. Soc. Chim.*, 1893, [iii], 9, 27) gave various experimental proofs that camphoric and isocamphoric acids contain, like lactic acid, two hydroxyl groups with different functions, one of them nearly alcoholic. Four esters were described, and a hypothesis regarding the constitution of camphor, with particular reference to the stereochemical formulæ of right and left rotating camphoric and isocamphoric acids, was illustrated with diagrams.

A method of analysis of isomeric xylenes and ethylbenzene was founded upon the fact that the xylenes, when treated with a large excess of bromine and a little iodine, form tetrabromo-substitution products nearly insoluble in light petroleum, and by that means separable from the dibromomethylbenzene formed under the same conditions. The tetrabromoxylenes can be oxidised quantitatively to the corresponding tetrabromophthalic acids by treatment at  $160$ — $170^{\circ}$  with bromine

and water, and the acids separated by precipitation (Friedel and Crafts, *Compt. rend.*, 1885, 101, 1218).

Armstrong and Miller published a description of the now well known and convenient mode of decomposition of sulphonic acids in sulphuric acid solution by means of steam, and the priority belongs to them; but before the method was made public, Friedel and Crafts had begun its study from a somewhat different point of view, and endeavoured to utilise the different temperatures at which the reaction takes place, in order to separate hydrocarbons, and in particular the hydrides of naphthalene from naphthalene (*Bull. Soc. Chim.*, 1884, [ii], 42, 66). Phosphoric acid was afterwards used as a solvent instead of sulphuric acid, in order to avoid the destructive and oxidising action of the latter (*Compt. rend.*, 1889, 109, 95).

Thiophosphates in well crystallised forms were obtained by heating the calculated quantities of phosphorus and sulphur with iron, aluminium, copper, lead, and silver to dull redness in sealed tubes. The general formula is  $M_4P_2S_8$ . Thioselenium salts were also obtained (Friedel, *Bull. Soc. Chim.*, 1894, [iii], 11, 1057; Friedel and Chabrié, *Bull. Soc. Chim.*, 1895, [iii], 13, 163).

An examination of fat from an Egyptian tomb showed that the glycerol had completely disappeared, apparently through oxidation. Palmitic and stearic acids were found unchanged, and azelaic and pimelic acid had been produced by oxidation (*Compt. rend.*, 1897, 124, 648).

#### *Mineralogical Researches.*

Friedel's work in mineralogy was of capital importance and marks a transition period in the history of that branch of science. After mineralogical cabinets had been filled with natural specimens, their sources duly noted, and when each species had been analysed, measured, and arranged, the old fashioned mineralogist seemed to have accomplished his task. To a collector of an antiquarian turn of mind, only those specimens which came from veins, druses, or rocky beds were of prime interest, whilst chemical or metallurgical products of similar composition, even when well crystallised, were set apart as new comers and not considered of equal rank with those whose landed title was well established. The geologist tried to describe the rocks in terms of mineral species, as chemical compounds are identified by the proportions of their elements; but only rarely were the conditions of formation of a species known or used to give testimony concerning the modes of formation of rocky strata. It was not duly appreciated that most crystalline rocks are a mixture of crystals with mother liquor, that purer specimens can be obtained by laboratory processes,

and that the essential constituents can be best determined by synthesis with pure materials.

Then came a period of synthetical mineralogy in which Friedel played an important part. It is evident that ideas regarding the igneous origin of an eruptive rock were confirmed if it contained the same crystalline species that could be observed in the slag of an iron furnace, and that the reproduction of minerals found in veins by sublimation or by crystallisation from water gave some evidence concerning natural processes. Moreover, some ideas concerning the effect of each of the different items contributing to the formation of a crystal can be gathered by the artificial production of the same crystal, under laboratory conditions of pressure, temperature, and presence or absence of water, each element in the experiment being subject to variation at will.

Friedel's equal skill as chemist and mineralogist enabled him to attack these problems to good purpose, and he pursued the subject with unswerving patience during his whole life, seeking to grow in a few days crystals which nature had passed ages in perfecting. Mineralogical problems were never excluded from his thoughts even at times when work in organic chemistry was progressing most successfully, and the delicate operations of these researches were performed by his own hands. New views of chemical composition, as, for instance, the hypothesis of the benzene ring, were immediately brought to bear on the formulæ of minerals, and the similarity of structure between the silicon and the carbon compounds with organic radicles, shown by his researches upon the silicon ethides, suggested new formulæ for silicates.

The details of his researches will show that many branches of experimental science were brought to bear upon his mineralogical work, and that from a very elevated standpoint he kept in view the paths by which mineralogy leads to geology, chemistry, and through delicate experiments in optical and pyro-electric phenomena, to the fundamental problems of molecular physics. His last illness cut short a research intended to offer final proofs of the necessary relation between rotatory power and the asymmetrical structure of carbon compounds.

Consciously or unconsciously he followed the lead of Pasteur in grouping his theories of the natural phenomena which came before him around a distinct conception of molecular arrangement from the point of view of a crystallographer.

The transference of his professorship from mineralogy to organic chemistry interrupted his work upon a mineralogical treatise of which the first part was published in 1893. This work was of elementary character and was particularly intended for the use of chemists. It

contains an exposition of geometrical crystallography, an original view of the principle of a chemical classification of minerals together with a discussion of the classifications of other authors, and an account of isomorphism and polymorphism. A second volume was to have followed containing descriptions of mineral species.

Friedel's papers were published in the *Comptes rendus*, the *Annales de Chimie et de Physique*, and *Bulletin de la Société Chimique* until, in 1878, he took part in founding the *Bulletin de la Société de Mineralogie*, and there published all his later work. He was most assiduous in attendance upon the meetings of the French Mineralogical Society and took an active part in its councils.

He published a lecture (*Revue Scientifique*, November 23rd, 1878) upon the work of his predecessor at the Sorbonne, Delafosse. Another lecture (*Revue Scientifique*, September 11th, 1880) gives a review of the methods previously employed for the artificial preparation of minerals. An address (*Bull. Soc. Miner.*, 1881, 4, 187), before the Mineralogical Society after the death of Henri St. Claire Deville, gives an account of the brilliant work of that chemist in the same field.

*Crystallography.*—At the time when Friedel began his mineralogical work, the pyro-electric phenomena in crystals did not appear to be always in accord with the ideas of symmetry and homogeneity of crystalline form developed by geometrical and optical studies. He undertook to show that the apparent anomalies were due to imperfect experiments, or to false interpretations, and with true scientific instinct commenced his review of the subject by the invention of improved methods of investigation. Of the two theses offered by him for the doctor's degree, one was upon pyro-electric phenomena in crystals. He verified Marbach's discovery of two varieties of pyrites of opposite thermo-electric signs; the two often united in the same crystal. It was supposed that external hemihedral forms were an essential characteristic pointing to the pyro-electric phenomena. Such forms would be non-superposable, but Friedel showed that they do not occur in parahemihedral crystals, which, like pyrites, give thermo-electric currents, although mathematically it is possible to conceive of their existence. In natural specimens, holoaxial hemihedral crystals alone show these non-superposable forms. He concluded that some structure which does not give an external sign was responsible for the electric phenomena of opposite signs, and he attributed them in parahemihedral crystals to a molecular arrangement along axes symmetrical about a centre, like the tertiary axes of pyrites, but so placed that their extremities cannot be superposed.

In crystals which conduct electricity like pyrites, these axes should mark the directions in which pyro-electric phenomena would manifest themselves. He investigated the subject experimentally, and succeeded in demonstrating these properties with certainty and regularity, but

only after having made thin, parallel-faced sections of the crystals. With entire crystals, irregular results are obtained which are confusing and have led different experimenters to erroneous conclusions. Friedel was the first to recognise that the strong currents set up when a crystal of pyrites is cooling are due to irregular rates of cooling in the mass of the crystal, and his first care was to eliminate such phenomena by making thin sections. He then succeeded in making a model with a thermo-electric couple of bismuth and antimony which imitated the phenomena occurring when crystals of pyrites are heated, and thus confirmed his theory that the crystals contain at the same time two kinds of molecular arrangement with non-superposable axes giving rise to thermo-electric currents of opposite signs.

He found that parahemihedral crystals which do not conduct an electric current, as apatite, for instance, show no pyro-electric phenomena, and concluded that in general the pyro-electric phenomena are not due to hemihedrism, when it can be referred to a centre, and that the property does not exist in pyrites in consequence of the parahemihedrism, but is induced only by the existence of the above-mentioned molecular arrangement about non-superposable axes of which no indication is given by external form.

He then examined the rare antihemihedral crystals which are good conductors, panabase and chalcopyrites, and discovered a regular flow of a pyro-electric current, as in tourmaline.

The interesting fact was shown that currents always flow in the same direction as those which would be produced by thermo-electricity in a system of metallic tetrahedrons of the same thermo-electric sign, and arranged in the same position as the crystal, and thus the hypothesis is suggested that pyro-electric phenomena in crystals may be due to the currents set up by tetrahedral elements. This first research of the young mineralogist was distinguished by a clear conception of a hypothesis accounting for certain phenomena and excluding others. It passed through the test of controversy, for in 1871 G. Rose published statements concerning pyrites and cobaltine, and asserted that external forms distinguished the two pyro-electric varieties. Friedel (*Compt. rend.*, 1874, 78, 508) pointed out errors in these observations, and maintained his previous conclusions by new experiments. A better method of heating crystals (*Bull. Soc. Miner.*, 1879, 2, 31) was described, in which a hot metallic ball was applied to a cold surface. When this new device for heating was applied to thin sections of crystals, pyro-electric currents were shown in topaz normal to the plane of cleavage, the experiment contradicting statements by Rose and Rose, and pyro-electric currents parallel to the tertiary axes in tourmaline.

Friedel had found pyro-electric phenomena in quartz: an observa-

tion which seemed to be at variance with the symmetry of this holoaxial crystal. Friedel showed that the pyro-electric direction corresponded only with binary axes, the edges of the prism being alternately of opposite sign. The fact, then, is in accord with the theory of symmetry; for there is no pyro-electricity displayed in the direction of the tertiary axis of which the two extremities are superposable, whilst it is shown where it would be expected in the direction of the binary axes, whose extremities are not superposable or symmetrical.

Subsequent investigations were made in conjunction with P. and T. Curie and with A. de Grammont, and these often took the form of a discussion with German crystallographers, because observations which appeared to contradict Friedel's views were again made by Hankel, and by Erman, Ries, and Rose.

The question required delicate handling, and the work of Friedel and his associates consisted in disengaging the phenomena which were purely pyro-electrical from others due to irregular internal tensions discovered by P. and T. Curie, and named by them piezo-electric; in other words, strains set up when a whole crystal cools irregularly are capable of producing electric currents.

In a paper published with T. Curie (*Bull. Soc. Miner.*, 1883, 6, 191), Friedel showed that, when all disturbing influences are eliminated, no pyro-electric currents can be obtained from crystals of the tertiary system, or with hexagonal crystals, like quartz, having three axes of hemimorphism in the same plane, or even in antihemidral crystals of the cubic system, in which the four axes of hemimorphism mutually compensate. Corroborative experiments were made with blende and with sodium chlorate. With reference to this theory, boracite presents a curious example in the two forms which it assumes according to the temperature. Above  $265^{\circ}$ , it is cubic and isotropic, and is not pyro-electric; at  $265^{\circ}$ , it becomes suddenly orthorhombic, and on cooling below this temperature pyro-electricity is manifested.

Later (*Bull. Soc. Miner.*, 8, 1885, 16), Friedel and T. Curie showed that a crystal of topaz, instead of being simply orthorhombic, as was held by Ries and Rose, and by other authorities, is composed of four clinorhombic individual crystals grouped about a central orthorhombic crystal. These five elements can be isolated by cutting, and a pyro-electric axis displayed parallel to the base, to which the central poles of Ries and Rose can be referred. He thus proved that the optical properties of topaz, pointing to an antihemihedral clinorhombic system grouped upon a rhombic centre, are in complete accord with the pyro-electric phenomena, namely, the central poles described above and a pyro-electric axis parallel with the axis of the prism. The twin formation of complementary crystals explains the accidental

occurrence of crystals whose two extremities have the same electric polarity.

Friedel and A. de Grammont (*Bull. Soc. Miner.*, 1895, 18, 75) studied the pyro-electric properties of scolecite, and found that a similar analysis could be made of the pyro-electric axes. They discovered in this mineral a peculiar arrangement of twin crystals, in which the two extremities show at their junction the same polarity, and consequently the macle formation cannot be explained by a rotation around an axis perpendicular to the plane of junction. This curious case of want of symmetry about the plane of junction has proved interesting with reference to a theory put forward later by Mallard.

Friedel proved that the two crystalline forms of hexachloride of benzene are in accord with the well-known theory of their "cis" and "trans" arrangement (*Bull. Soc. Chim.*, 1891, [iii], 5, 130). He developed the theory to show that tertiary symmetry is indicated for the *cis*- and binary for the *trans*-form. A calculation of the necessary ratio in which the two forms will be generated during saturation with chlorine and disruption of carbon bonds, compared with experimental results, confirmed the identification of each form.

This account would not be complete without a reference to the discussions between Friedel, Mallard, and Wyruboff (*Bull. Soc. Miner.*, 1886, 9, 121). Friedel insisted upon the capacity of crystallising together as a final test of isomorphism in opposition to views of Mallard, who was prepared to extend very widely the definition of isomorphous substances.

The *Bulletin de la Société de Mineralogie* contains a considerable number of Friedel's descriptions and measurements of mineral species.

*Artificial Production of Minerals.*—The synthesis of atacamite (*Compt. rend.*, 1873, 77, 211), four years later than the thesis upon pyro-electric phenomena, was effected by the action of ferric chloride upon cuprous oxide in sealed tubes at 250°.

Friedel and J. Guérin (*Ann. Chim. Phys.*, 1876, [v], 8, 24) studied various titanium compounds and obtained titanium sesquioxide in the form of rhombohedral crystals, isomorphous with oligist and ilmenite. Among the much disputed formulæ for the latter mineral, preference is given to  $\text{FeTiO}_3$ , in which iron and titanium are mutually replaceable as silicon can replace titanium in its higher stage of oxidation. Crystallised rutile was also obtained by the action of titanium chloride on ferrous oxide at a high temperature.

The publication of the most important series of syntheses was begun in 1879 (*Bull. Soc. Miner.*, 2, 113). Most of the work done between



this date and 1887 was in collaboration with Edmund Sarasin and was published in full in the *Arch. Sci. phys. et natur. de Genève*, 1892.

The required materials, together with water, were heated in the very stout steel tube lined with platinum, already described. High pressure and a temperature of  $500^{\circ}$ , corresponding in the earth's crust to a considerable depth of rocky strata, were reached, and the results were interpreted with reference to geological theories. The use of a platinum tube guaranteed the purity of the compounds. The crystals produced within the few days devoted to an experiment were small and required care and skill in measurement to identify them with known species, but they were usually well defined and uniform in their aspect.

The first published observation of Friedel and Sarasin (*Bull. Soc. Miner.*, 1879, 2, 113) described the formation of beautiful prisms of quartz with pyramidal terminations when an excess of amorphous silica was heated with caustic potash. These crystals, which are easily measurable, appeared frequently together with other minerals in later syntheses. Quartz with a new macle was observed among the crystals (*Bull. Soc. Miner.*, 1888, 2, 29).

The formation of orthose feldspar (Friedel and Sarasin, *Bull. Soc. Miner.*, 1879, 2, 158; 1880, 3, 23; 1881, 4, 171; *Compt. rend.*, 1881, 92, 1374), under well defined conditions, threw new light upon the mode of formation of the so-called acid rocks. Friedel, with scrupulous care, repeated his experiments under various conditions during three years before he affirmed the absolute identity of the artificial and natural species. The materials were silicates of potassium and aluminium with a large excess of water. Quartz is usually formed as well, and when a higher temperature is employed tridymite also, showing that silica naturally crystallises in these two forms at corresponding temperatures. The bearing of these facts upon the mode of genesis of granite was pointed out.

Albite and analcime are formed by a similar process when sodium instead of potassium silicate is used. No intermediate feldspar containing the two bases could be obtained and the natural minerals having such a composition are probably mixtures (*Compt. rend.*, 1883, 97, 290).

The action of alkalis and sodium silicate on the zeolites was investigated by Friedel and Sarasin (*Bull. Soc. Chim.*, 1884, [ii], 41, 593). Friedel proposed a general formula for this mineral group and sought to verify it by transforming its different members. Sodium can be substituted for calcium in laumontite with formation of analcime. In this reaction, there is also formed a mineral nearly related to mesotype, and it was shown that the same mineral was

obtained by subjecting natural mesotype to the action of the same reagents.

Friedel, with his son, Georges Friedel, pursued a similar series of investigations upon the metamorphosis of mica. Many attempts were made to obtain white mica in presence of alkalis, but it was found that mica is not stable under these conditions, that at 400—500° it is easily decomposed by the alkalis, giving rise to other species, and when silicates or other salts are added the products of transformation resemble the well known series found at Somma.

When the micas are treated with alkalis alone, substitutions of one base for another could be obtained.

Muscovite (*Bull. Soc. Miner.*, 1890, 13, 129), at 400—500°, in presence of dilute sodium hydroxide, is transformed without residue into fine crystals of nepheline, so pure that the constitution of this mineral could be definitely established as an orthosilicate,  $\text{AlNaSiO}_4$ . The transformation seems to consist in substituting sodium for potassium and hydrogen in muscovite without destroying the molecular arrangement. It was found impossible, however, to obtain a nepheline containing potassium without sodium. Mica is transformed into orthose by heating with potassium silicate and potassium hydroxide. Also, when a suitable proportion of silica was taken, a quadratic form of amphigene was produced without icositetrahedral grouping. This synthesis is interesting from a crystallographical point of view, because the form which appears at a temperature lower than that at which the mineral becomes cubic and isotropic shows parahemihedrism not recognised in natural specimens, and the pseudo-icositetrahedral form of the natural crystals is explained by a junction of three crystals with trirectangular axes.

Sodalite (*Bull. Soc. Miner.*, 1890, 13, 180) was formed by heating mica with sodium chloride and hydroxide. It had the same composition,  $3\text{SiO}_4\text{AlNa} + \text{NaCl}$ , no matter what proportion of salt was added, and was identical with Somma sodalite.

Anorthite (*Bull. Soc. Miner.*, 1890, 13, 230) can be obtained by heating mica with calcium chloride and hydroxide. The crystals are well formed, and free from potassium.

Mica is transformed by calcium hydroxide into a hydrated silicate of the cubic system not found in nature.

A mixture of sodium sulphate and hydroxide converts white mica into a new compound,  $6\text{SiO}_4\text{AlNa}_2\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . The crystals are transparent, and isomorphous with those of nepheline, cancrinite, and microsommite. A mineral like the preceding, but with one molecular proportion of water, is formed in small quantity, also a little black mineral. Muscovite mica, heated with sodium carbonate and hydroxide, gives a mineral like cancrinite,  $6\text{AlNaSiO}_4 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ .

Friedel and Sarasin (*Bull. Soc. Miner.*, 1887, 10, 737), prepared topaz by heating aluminium fluorosilicate. Quadratic crystals of aluminium fluoride are also formed. Friedel pointed out an error in the usual method of analysing topaz, arising from a loss of aluminium fluoride, as well as silicon fluoride, when the mineral is heated in a platinum crucible. The composition, instead of being variable, as was supposed, is constant, and corresponds with that required for the formula  $\text{Al}_2\text{F}_2\text{SiO}_4$ .

The following list comprises other syntheses of minerals achieved by Friedel and Sarasin: Libethenite (*Bull. Soc. Miner.*, 1879, 2, 157); hopeite (*ibid.*, 153); copper selenite (*ibid.*, 1881, 4, 176); phosgenite (*ibid.*, 176); leadhillite (*Bull. Soc. Chim.*, 1883, [ii], 39, 626); calcite (*Bull. Soc. Miner.*, 1885, 8, 304); mellite was synthesised by Friedel and Balsahn (*Bull. Soc. Miner.*, 1891, 14, 26); and Friedel prepared cumengeite (*Bull. Soc. Miner.*, 1892, 15, 96), bolcite (*ibid.*, 1894, 17, 6), and martite (*ibid.*, 1894, 17, 150).

From an examination of diamonds contained in native iron from Cañon Diablo (*Compt. rend.*, 1893, 116, 224), Friedel concluded that their formation had been accompanied by that of sulphide of iron at a relatively low temperature. He attempted to obtain crystallised carbon by the action of sulphur on a highly carburetted cast iron at 450—500°. A black powder was obtained hard enough to scratch corundum, but in too small quantity to be analysed. This essay is particularly interesting, as it seems to imitate a natural process.

The following new species of minerals were discovered by Friedel: Wurtzite (*Compt. rend.*, 1861, 52, 983); adamine (*Compt. rend.*, 1866, 62, 692); and delafossite (*Compt. rend.*, 1873, 77, 211); whilst carnotite was described by Friedel and Cumenge (*Bull. Soc. Miner.*, 1899, 22, 26).

The *Bulletin de la Société de Mineralogie* from 1879 to 1894 contains numerous descriptions of minerals from different localities. Many of these investigations were made by Friedel in connection with his duties as Curator of the Mineralogical Cabinet of the School of Mines, which led him constantly to examine minerals from new localities, and he was at all times actively employed in adding new specimens to that fine collection.

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XC.—*Diphenyl- and Dialphyl-ethylenediamines, and their Nitro-derivatives, Nitrates, and Mercurichlorides.*

By WILLIAM SLOAN MILLS, B.A., Demonstrator of Chemistry in the Queen's College, Galway.

HAVING obtained, in the course of some experiments, a quantity of diphenylethylenediamine by the interaction of aniline and ethylene dibromide (Hofmann, *Proc. Roy. Soc.*, 1858, 9, 277; 1859, 10, 104; Morley, *Ber.*, 1879, 12, 1794), I endeavoured to obtain with it several reactions of which there appears to be no previous record. The result of preliminary experiments showed that it admitted of direct nitration, forming nitro-derivatives, and that it formed a well-defined nitrate and mercurichloride. I determined, therefore, to try to isolate these compounds, and to extend the inquiry to some, at least, of the homologous alphyethylenediamines, and, in the case of the nitro-derivatives, to compare them with those already known, but obtained by other reactions.

*Nitration of Diphenylethylenediamine.*—The material used in these experiments was recrystallised from dilute alcohol; it softened at  $61.5^{\circ}$  and melted at  $63^{\circ}$ . It was dissolved in glacial acetic acid, forming about a 5 per cent. solution, and to this was gradually added concentrated nitric acid. The mixture was kept in constant agitation, and heat was applied at first until action commenced, when cooling was necessary, to prevent its becoming too violent. In the first instance, the solution assumed a dark olive-brown colour, which, as the reaction proceeded, changed to a deep reddish-brown, and finally the colour became much lighter. A yellow precipitate appeared towards the end of the reaction, and on continued application of heat, after the completion of the nitration, this increased in quantity. It was washed first with hot glacial acetic acid, and then with water, and dried at  $110^{\circ}$ . It melted at  $307\text{--}308^{\circ}$  (corr.), and, on analysis:

0.3376 gave 59.5 c.c. moist nitrogen at  $15^{\circ}$  and 769.4 mm.  $N = 20.9$ .

$C_{14}H_{12}O_8N_6$  requires  $N = 21.47$  per cent.

This tetranitrodiphenylethylenediamine,  $C_6H_4[NH \cdot C_6H_3(NO_2)_2]_2$ , is similar in appearance and solubility to that prepared by Jedlicka (*J. pr. Chem.*, 1893, [ii], 48, 202), by the interaction of 1-bromo-2:4-dinitrobenzene and ethylenediamine, for which the melting point  $302\text{--}303^{\circ}$  is given, and is therefore identical with it. The substitution on the benzene rings is therefore probably  $[N:NO_2:NO_2 = 1:2:4]$ . The liquid separated from the above com-

pound, a yellow powder is precipitated. This precipitate was pressed between blotting paper and dried on a porous plate in a vacuum over sulphuric acid. It melted at  $85^{\circ}$ , and proved to be an isomeric *tetra-nitrodiphenylethylenediamine*. On analysis :

0.2225 gave 0.8477  $\text{CO}_2$  and 0.0603  $\text{H}_2\text{O}$ .  $\text{C}=42.61$  ;  $\text{H}=3.01$ .

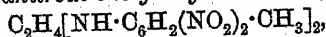
0.4201 „ 77 c.c. moist nitrogen at  $14^{\circ}$  and 757 mm.  $\text{N}=21.46$ .

$\text{C}_{14}\text{H}_{12}\text{O}_8\text{N}_6$  requires  $\text{C}=42.85$  ;  $\text{H}=3.06$  ;  $\text{N}=21.47$  per cent.

This compound is very soluble in acetone, ethyl acetate, or glacial acetic acid. On boiling the solution in acetone, the substance undergoes a remarkable metastatic change, being converted into the isomeride melting at  $307\text{--}308^{\circ}$  (corr.), described above.

*Nitration of Di-o-tolythylenediamine.*—In the preparation of di-o-tolythylenediamine, the directions of Mauthner and Suida (*Monatsh.*, 1886, 7, 230), and of Bischoff and Hausdörfer (*Ber.*, 1890, 23, 1982), were followed in the main. The following method, which involves a slight modification, gives a yield of about 25 per cent. of that calculated for a simple reaction. Two mols. of o-toluidine, made into a paste with sodium carbonate, are heated in a flask provided with reflux condenser, and one mol. of ethylene dibromide added, with constant shaking. During the process, which lasts for half an hour, more sodium carbonate is added, and the temperature is kept at about  $130^{\circ}$ . The flask is then placed in a paraffin bath at  $160^{\circ}$  for about half an hour. The residue is washed with water and extracted with light petroleum, from which crystals are deposited on spontaneous evaporation. These are reduced to a fine powder and extracted with alcohol. A white residue remains, which, when recrystallised from boiling alcohol, melts at  $155\text{--}157^{\circ}$ , and is doubtless the diethylenedi-o-tolyldiamine obtained by Mauthner and Suida under similar circumstances, which, when purified, was found by them to have a somewhat higher melting point. To the solution in alcohol, dilute nitric acid is gradually added, the vessel containing the mixture being surrounded with cold water, when a crystalline precipitate of the nitrate gradually separates. This salt will be more fully described. To prepare the base, these crystals are powdered and mixed with sodium carbonate, and the mixture made into a thin paste with sodium hydroxide solution. This paste, warm from the reaction, is extracted with light petroleum, which on slow evaporation, yields colourless crystals of the pure base. It melts at  $70.5^{\circ}$ , and the same melting point was found in the case of several different preparations, and remained constant after further recrystallisation. Previous investigators have observed higher melting points, namely,  $78^{\circ}$  (Mauthner and Suida) and  $75\text{--}76^{\circ}$  (Bischoff and Hausdörfer). The nitration was effected in the manner described for the phenyl homologue, and similar changes of colour are observed during the

reaction. No precipitate appears, but when water is poured into the solution, an amorphous, yellow precipitate falls, which softens and agglomerates to a semi-solid mass on heating the mixture. This is removed, and when cooled is powdered and extracted with hot glacial acetic acid, a small portion being allowed to remain undissolved; this solution is precipitated by water, and the precipitate washed by water and dried. This *tetranitrodi-o-tolylothylenediamine*,



melts at 78—79°. On analysis:

0.2406 gave 0.4068  $\text{CO}_2$  and 0.0822  $\text{H}_2\text{O}$ .  $\text{C} = 46.11$ ;  $\text{H} = 3.79$ .

0.5894 ,, 98.5 c.c. moist nitrogen at 13° and 774.5 mm.  $\text{N} = 20.12$ .

$\text{C}_{16}\text{H}_{16}\text{O}_8\text{N}_6$  requires  $\text{C} = 45.69$ ;  $\text{H} = 3.81$ ;  $\text{N} = 20.0$  per cent.

In one experiment, whilst attempting to recrystallise the nitro-derivative from hot ethyl acetate, it was found to have undergone a change similar to that observed in the case of the corresponding phenyl homologue. The melting point rose from 78—79° to 178—180°. This compound is doubtless an isomeric *tetranitro-o-tolylothylenediamine*. It is an amorphous, yellow powder like the isomeride analysed.

*Nitration of Di-m- and Di-p-tolylothylenediamines.*—Di-*m*-tolylothylenediamine, which was obtained by Francis (Trans., 1897, 71, 426) by treating the hydrochloride in alcoholic solution with alcoholic sodium hydroxide, can be prepared more readily in large plates by the method described in this paper for the ortho-isomeride. It melts at 58.5°. When nitrated in the manner described for the ortho-isomeride, a yellow powder is obtained which melts at 57°. On analysis:

0.3152 gave 55.5 c.c. moist nitrogen at 17° and 763.5 mm.  $\text{N} = 20.51$ .

$\text{C}_{16}\text{H}_{16}\text{O}_8\text{N}_6$  requires  $\text{N} = 20$  per cent.

The *tetranitrodi-m-tolylothylenediamine*, resisted several attempts at further purification.

Di-*p*-tolylothylenediamine is prepared and purified in the manner similar to its ortho- and meta-isomerides. It melts at 95°.

During its nitration, a dark green to a brown colour develops, and, on shaking the mixture, a mass of fine, orange-red crystals separates. These are washed with acetic acid and then boiled with alcohol, in which they are almost insoluble. The *dinitrodi-p-tolylothylenediamine*,  $\text{C}_2\text{H}_4[\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CH}_3]_2$  melts at 195—196° (corr.). On analysis:

0.1844 gave 25.8 c.c. moist nitrogen at 16° and 769.5 mm.  $\text{N} = 16.51$ .

$\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_4$  requires  $\text{N} = 17.0$  per cent.

Wittmann and Hager (Ber., 1884, 17, 778) obtained the same compound from the interaction of ethylene dibromide and *m*-nitro-*p*-toluidine.

*Preparation of Nitrates and Mercurichlorides of Diphenyl- and Ditolylethylenediamine.*—When the diphenyl base is dissolved in hot dilute nitric acid and the solution allowed to cool, an abundant deposit of colourless needles of *diphenylethylenediamine nitrate*,  $C_2H_4(NH \cdot C_6H_5)_2 \cdot 2HNO_3$ , occurs; this melts to a dark liquid at  $164.5^\circ$  (corr.). On analysis:

0.2063 gave 0.3822  $CO_2$  and 0.1084  $H_2O$ . C = 50.52; H = 5.83.

0.2546 „ 36.8 c.c. moist nitrogen at  $13^\circ$  and 775.5 mm. N = 17.4.

$C_{14}H_{18}O_6N_4$  requires C = 49.7; H = 5.34; N = 16.6 per cent.

The ditolylethylenediamine nitrates are obtained by adding dilute nitric acid to solutions of the bases in alcohol. The mixtures are kept cool, when crystalline precipitates are obtained, which are purified by recrystallisation from alcohol.

*Di-o-tolylethylenediamine nitrate* melts to a dark liquid at  $152^\circ$  (corr.). On analysis:

0.4029 gave 53 c.c. moist nitrogen at  $11^\circ$  and 758.2 mm. N = 15.63.

$C_{16}H_{22}O_6N_4$  requires N = 15.33 per cent.

*Di-p-tolylethylenediamine nitrate* melts at  $166.5^\circ$  (corr.). A specimen, probably not quite pure, was analysed:

0.3467 gave 48 c.c. moist nitrogen at  $16^\circ$  and 753 mm. N = 15.99.

*Di-m-tolylethylenediamine nitrate* melts at  $153^\circ$  (corr.). On analysis:

0.2551 gave 33.8 c.c. moist nitrogen at  $14^\circ$  and 746.5 mm. N = 15.30.

To prepare the mercurichlorides, alcoholic solutions of mercuric chloride are added to alcoholic solutions of the bases in molecular proportion, when crystalline precipitates separate slowly, on standing, except in the case of the *m*-tolyl compound.

*Diphenylethylenediamine mercurichloride*,  $C_2H_4(NH \cdot C_6H_5)_2 \cdot HgCl_2$ , melts at  $129^\circ$  (corr.) and consists of well-formed, colourless, rhombic plates. On analysis:

0.2277 gave 0.2886  $CO_2$  and 0.0784  $H_2O$ . C = 34.56; H = 3.82.

0.314 „ 0.1515  $HgS$ . Hg = 41.62.

1.0552 „ 0.505  $HgS$ . Hg = 41.25.

$C_{14}H_{16}N_2Cl_2Hg$  requires C = 34.78; H = 3.31; Hg = 41.4 per cent.

Careful heating is required in the combustion of the mercurichloride to prevent distillation of mercury into the drying tubes.

*Di-o-tolylethylenediamine mercurichloride*,

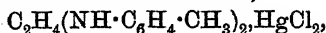
$C_2H_4(NH \cdot C_6H_4 \cdot CH_3)_2 \cdot HgCl_2$ ,

crystallises in small, rhombic plates, and melts at  $110^\circ$ . On analysis:

0.559 gave 0.259  $HgS$ . Hg = 39.9.

$C_{16}H_{20}N_2Cl_2Hg$  requires Hg = 39.16 per cent.

*Di-p-tolythylenediamine mercurichloride,*



crystallises in white, feathery flakes and melts at  $133^\circ$  (corr.). On analysis:

0.5639 gave 0.256 HgS. Hg = 39.12 per cent.

*Di-m-tolythylenediamine mercurichloride* melts at  $79-80^\circ$ . This mercurichloride is different in its behaviour from the ortho- and para-compounds. It is not precipitated, as they are, on mixing solutions of the bases with mercuric chloride, but is obtained by spontaneous evaporation of the mixed solutions, when it appears as rosettes of minute crystals. On analysis, too, it gives 35.9 per cent., and in another experiment 35.1 per cent. of mercury instead of 39.16 per cent. Its constitution for the present, therefore, is uncertain.

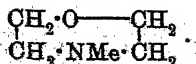
I wish to express my indebtedness to Professor Senier for numerous suggestions made during the course of this inquiry.

## XCI.—*Researches on Morphine. Part I.*

By S. B. SCHRYVER and FREDERIC H. LEES.

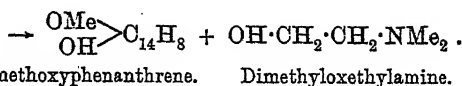
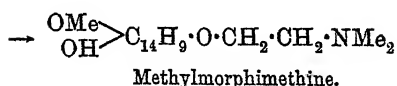
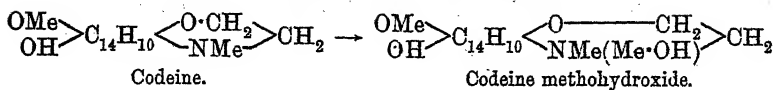
MORPHINE is a subject of considerable interest from a twofold standpoint, namely, the chemical and the pharmacological. Our knowledge of the subject from the chemical side is due mainly to L. Knorr and Vongerichten.

Older researches have shown that morphine is a phenanthrene derivative, and contains two hydroxyl groups, one of a phenolic character, the other alcoholic. On treatment with methyl iodide (two molecular proportions) in the presence of sodium ethoxide, it yields the methiodide of its methyl ether (codeine), and the hydroxide, derived from this compound, codeine methohydroxide,  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}\cdot\text{OMe}\cdot\text{CH}_3\text{OH}$ , on warming with alkalis loses the elements of water, and is converted into methocodeine or methylmorphimethine,  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}(\text{OMe})\cdot\text{CH}_3$ . This substance is a tertiary base, and on heating with acetic anhydride is converted into the acetyl derivative of dimethyloxethylamine,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , and the acetyl derivative of a hydroxymethoxyphenanthrene,  $\text{OH}\cdot\text{C}_{14}\text{H}_8\cdot\text{OMe}$ . An isomeric product,  $\beta$ -methylmorphimethine, is produced at the same time. The production of acetyl dimethyloxethylamine in this way is characteristic of derivatives of the closed ring compound, *N*-methylmorpholine,

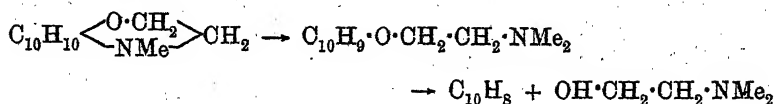




Knorr represents the reactions by the following formulæ :

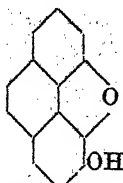


The synthetical base, naphthalanmorpholine, undergoes similar transformations :

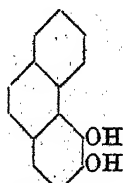


(*Ber.*, 1889, 22, 181, 1113, 2081 ; 1894, 27, 1149 ; 1899, 32, 737, 742 ; *Annalen*, 1898, 301, 1 ; 1899, 307, 171).

Vongerichten's more recent researches deal principally with the nitrogen-free decomposition products of morphine (*Ber.*, 1897, 30, 355, 2441 ; 1898, 31, 51, 3198 ; 1899, 32, 1521, 2379 ; 1900, 33, 352). He shows that the  $\beta$ -methylmorphimethine discovered by Knorr (*Ber.*, 1894, 27, 1149) is not acted on by acetic anhydride, but that its methiodide on treatment with alkalis readily decomposes, giving as a main product a monohydroxyphenol,  $\text{C}_{14}\text{H}_9\text{O}_2$  (morphenol), which readily reduces to the dihydroxyphenanthrene (morphol), of which the methyl ether was obtained by Knorr, as just described. As a result of his researches, Vongerichten assigns the two following formulæ to morphenol and morphol respectively :



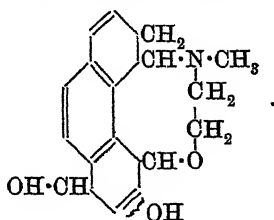
Morphenol.



Morphol.

These formulæ become of special interest in view of the recent researches of Pschorr and his collaborators on the synthesis of the hydroxyphenanthrenes, and from the results we can obtain some clue to the positions which the hydroxyl groups and the morpholine residue

occupy in the phenanthrene nucleus. Knorr and Vongerichten both assign to morphine the following probable constitution:



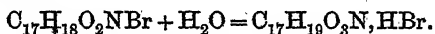
There still remains to be determined, however, the exact points to which the various hydroxyls remain attached, as well as the relationship existing between the  $\alpha$ -morphimethine and  $\beta$ -morphimethine derivatives. By substituting the alcoholic hydroxyl by halogen or other groups or elements, and subjecting these products to the action of various reagents, it was expected that a new series of phenanthrene products might be obtained, which would further elucidate the constitution of morphine.

The second point of interest was to determine the influence of such substitutions on the physiological character of the morphine. Owing to the fact that the methyl ether of morphine (codeine), which occurs amongst the opium alkaloids, has long been employed in medicine, this aspect of the research seemed to be of some practical importance. The investigations hitherto undertaken with the view of determining the influence of substitution on the physiological action of morphine have been confined almost entirely to the preparation of the alkyl and acyl derivatives formed by the substitution of the hydrogen of the hydroxyl groups by various radicles (Stockman and Dott, *Brit. Med. Journ.*, 1890, ii, 189; von Mering, *Merck's Annual Report*, 1898, pub. March, 1899; Dreser, *Pflüger's Archiv*, 1898, 72, 485). The compounds investigated have all a modified narcotic action, and as the result of these researches various products have been placed on the market, such as "dionin" (ethylmorphine hydrochloride); "heroin" (diacetylmorphine hydrochloride); "peronin" (monobenzylmorphine hydrochloride). Furthermore, apomorphine, C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>N, discovered many years ago by Matthiessen and Wright, has an emetic action, and is not usually employed as a narcotic; its chemical relationship to morphine, from which it is prepared by the action of hydrochloric acid, and from which it differs so considerably in physiological action, remains yet to be determined.

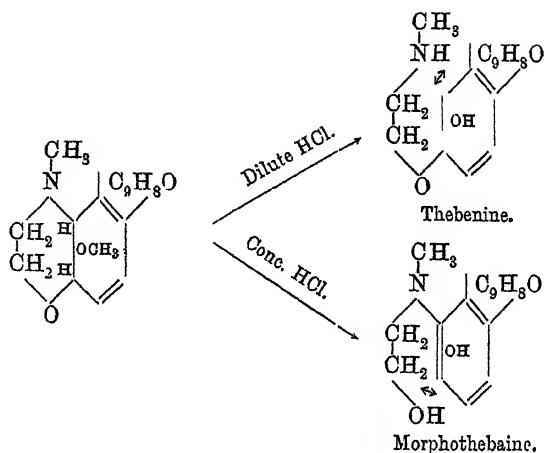
When morphine is treated with phosphorus trichloride, it yields a crystalline base, C<sub>17</sub>H<sub>15</sub>O<sub>2</sub>NCl, in which, as it yields only a mono-acetyl derivative, the hydroxyl is replaced by chlorine. This product

is designated *chloromorphide*. In a similar way, by treating morphine with phosphorus tribromide, a *bromomorphide* is obtained. On treating chloromorphide with tin and hydrochloric acid, the chlorine is replaced by hydrogen, and the hydrochloride of a base,  $C_{17}H_{19}O_2N$ , is formed, which is called *deoxymorphine* in this paper. *None of these products has a narcotic action, even when given in grain doses, the usual dose for morphine being about  $\frac{1}{8}$  grain.*

This result seemed at first sight astonishing in view of the fact that the simple synthetical base naphthalanmorpholine, of which the formula is given above, has almost the same physiological action as morphine (Leubuscher, *Annalen*, 1899, 307, 172). On further investigating the halogen products, it was found that this non-narcotic action may be assigned to purely chemical causes. On warming a neutral solution of chloromorphide hydrochloride on the water-bath, it rapidly becomes strongly acid. The free bases furthermore, on heating with water, rapidly decompose and go into solution, giving in the case of bromomorphide the hydrobromide of a base, according to the following equation :



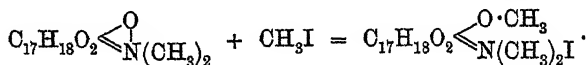
The product, however, is not morphine, but a crystalline, isomeric, non-narcotic base which we have called *isomorphine*. Several of its salts and derivatives have been prepared and contrasted with those of morphine. Like morphine, it is laevorotatory, but more strongly so, and the salts are very much more readily soluble in water. On treatment with phosphorus trichloride, it yields a product, which has not yet been fully investigated, but which is certainly not chloromorphide. Unlike morphine, it does not reduce gold chloride readily, and as it is the only product produced when bromomorphide is treated with water, and like morphine is laevorotatory, it is highly improbable that it is merely a stereoisomeride. The problem now remains to determine the chemical relationship to morphine, and in this investigation we have already certain facts to guide us. It is known that when thebaine, which is also a morpholine derivative, is treated with hydrochloric acid, a methoxyl group is hydrolysed, and one of two products is formed, according to the conditions of experiment, thebenine being obtained with dilute hydrochloric acid, but morphothebaine with the concentrated acid (Freund, *Ber.*, 1897, 30, 1357; 1899, 32, 168). Knorr has suggested an explanation of the two reactions by means of the following formulæ (*Ber.*, 1899, 32, 746) :



It seems likely that chloromorphide or bromomorphide, on treatment with water, behave in a similar manner.

With the object of determining the constitution of isomorphine, work is now proceeding in various directions, and preliminary results are recorded in the following pages.

On treatment of the methiodide with acetic anhydride, only a minute quantity of a nitrogen-free product is obtained, which has the same melting point as the phenanthrene derivative obtained in a similar way from morphine methiodide. This fact should exclude a product analogous in constitution to that given above to thebenine, where the morpholine ring is broken at the nitrogen, for derivatives of this character, as Knorr has shown, readily yield nitrogen-free products on treatment with acetic anhydride. Further, the methohydroxide of isomorphine, obtained by the action of silver sulphate on the iodide and subsequent treatment of the sulphate thus produced by barium hydroxide, acts in a way quite analogous to morphine methohydroxide, which Vongerichten has shown to have a phenol-betaine constitution (*Ber.*, 1897, 30, 355), forming a deliquescent, crystalline hydrate; this, when left in a vacuum, yields a powder which combines on warming with methyl iodide with the opening up of an anhydride ring and the formation of the methiodide of a methyl ether.



Such a reaction is also possible with isomorphine, and it therefore does not follow that the latter is a secondary base, because the product obtained by treating its methiodide with silver hydroxide (silver sulphate and barium hydroxide) unites directly with methyl iodide.

The investigation of the iodide produced in this way should throw further light on the constitution of isomorphine, and researches are being prosecuted in this direction.

It seems, however, quite likely that isomorphine is analogous in its constitution to morphothebaine. The results are also interesting as they indicate that a slight change in the morphine molecule may render the morpholine ring unstable, and thus account for the non-narcotic action of such substances as chloromorphide and bromomorphide, in view of the fact that simple synthetical morpholine derivatives like naphthalanmorpholine act physiologically like morphine. The further study of the decomposition products of morphine should offer also a chemical *rationale* for the physiological classification of narcotics like codeine, thebaine, morphine, &c., such as has been attempted by Bradbury and others (see Croonian Lectures, Royal College of Physicians, *British Medical Journal*, or *Lancet*, 1899).

#### EXPERIMENTAL.

##### *Chloromorphide.*

Twenty grams of morphine, previously dried at  $120^{\circ}$ , are introduced into a wide-mouthed flask connected with a long air condenser. Phosphorus trichloride is then added in sufficient quantity to soak through the solid mass of morphine. After a few moments, a vigorous reaction takes place, and the mixture froths up. The reaction is completed by heating for 3—4 hours on a water-bath. The contents of the flask at the end of this time form a homogeneous, light-brown, pasty mass. This is then disintegrated with alcohol, in which it gradually dissolves, and after a short time chloromorphide hydrochloride separates out if only a small quantity of alcohol is employed. It is advisable, however, to add enough alcohol to keep the hydrochloride in solution when the mixture is slightly warmed. It is then diluted with water, made alkaline with sodium carbonate, and extracted four times with chloroform. The chloroform solution is washed several times with water to free it from alcohol, rapidly dried over calcium chloride, filtered, and the chloroform removed by distillation; the residue consists of white, glistening crystals of chloromorphide suspended in ethyl phosphite. The crystals are collected, washed with alcohol, and being already very nearly pure can be employed for further work without any additional purification. From 12—14 grams of base are generally obtained in this way, and a further quantity can be isolated from the syrupy filtrate by dissolving it in pure dry ether and passing dry hydrogen chloride into this solution. A white precipitate of the hydrochloride of the base is obtained; this deliquesces in the air to a pasty mass, which on further

standing gradually becomes hard, and can be readily purified by recrystallisation.

Chloromorphide is a beautifully crystalline product which melts with decomposition at  $190^{\circ}$ . It is scarcely soluble in ether, although, when freshly precipitated from a solution of its salts by alkalis, it dissolves readily in this solvent, but separates out again almost immediately in a brilliant, crystalline form. It is easily soluble in chloroform, and in methyl and hot amyl alcohols, but only sparingly so in boiling ethyl alcohol. It is insoluble in benzene, light petroleum, and most other organic solvents.

0.1707 gave 0.4214  $\text{CO}_2$  and 0.0917  $\text{H}_2\text{O}$ .  $\text{C} = 67.32$ ;  $\text{H} = 5.96$ .

0.1290 „ 0.3180  $\text{CO}_2$  „ 0.0715  $\text{H}_2\text{O}$ .  $\text{C} = 67.22$ ;  $\text{H} = 6.15$ .

0.2830 „ 11.8 c.c. moist nitrogen at  $20^{\circ}$  and 760 mm.  $\text{N} = 4.77$ .

0.3702 „ by Carius' method, 0.1731  $\text{AgCl}$ .  $\text{Cl} = 11.57$ .

$\text{C}_{17}\text{H}_{18}\text{O}_2\text{NCl}$  requires  $\text{C} = 67.4$ ;  $\text{H} = 5.93$ ;  $\text{Cl} = 11.68$ ;  $\text{N} = 4.61$  per cent.

A determination of the specific rotation in methyl alcohol gave the following result:

$$\alpha_D = -2^{\circ}9', l = 1 \text{ dm.}, c = 0.573, [\alpha]_D = -375.2^{\circ}.$$

*Chloromorphide Hydrochloride* is prepared from the base by grinding it up in a mortar with a slight excess of 10 per cent. hydrochloric acid. A pasty mass is at first formed, but on grinding it is rapidly converted into a snow-white powder, which can be readily filtered off from the mother liquor. Its aqueous solution is unstable, for reasons already described, and it can only be recrystallised from water with considerable loss. It dissolves readily in hot alcohol, and on slowly cooling separates in hard crusts of diamond-like, highly refractive, anhydrous crystals.

0.2456 gave, by Carius' method, 0.1969  $\text{AgCl}$ .  $\text{Cl} = 19.84$ .

$\text{C}_{17}\text{H}_{18}\text{O}_2\text{NCl}, \text{HCl}$  requires  $\text{Cl} = 20.88$  per cent.

Its aqueous solution is very strongly laevorotatory.

$$\alpha_D^{20} = -5^{\circ}16', l = 1 \text{ dm.}, c = 1.67, [\alpha]_D^{20} = -315.3^{\circ}.$$

The *hydrobromide* is prepared in the same way as the hydrochloride, and is similar in its properties. Neither in this salt nor in the hydrochloride could the halogen acid combined with the base be determined by direct titration with silver nitrate, as the end reaction was not sharp, probably owing to the ease with which the salt is decomposed. The salt used for analysis was recrystallised from absolute alcohol.

0.3241 gave, by Carius' method, 0.2716 of mixed  $\text{AgCl}$  and  $\text{AgBr}$ .

$\text{C}_{17}\text{H}_{18}\text{O}_2\text{NCl}, \text{HBr}$  requires 0.2793 gram.

The specific rotation of the salt recrystallised from alcohol gave the following result:

$$\alpha_D^{18} = -4^{\circ}26', l = 1 \text{ dcm.}, c = 1.65, [\alpha]_D^{20} = -268.6^{\circ}.$$

*Examination of Mother Liquors from preparation of Chloromorphide.*

—After extracting the alkaline liquors with chloroform until nothing more went into solution, the aqueous residue always gave a fairly copious precipitate with Mayer's reagent, and as the maximum yield of chloromorphide did not amount to more than 75 per cent. of the theoretical, a certain amount of another alkaloid must be present. The alkaline mother liquors were therefore carefully neutralised with dilute hydrochloric acid, and evaporated to a small bulk. On evaporation, the solution became acid, and more alkali was added from time to time to keep it perfectly neutral. The mixture was evaporated to dryness, and the residue extracted with absolute alcohol in a Soxhlet apparatus to separate the alkaloidal salt from the purely inorganic residue. After distilling off the alcohol, the residue was dissolved in water, the solution boiled with a little animal charcoal to decolorise it, made alkaline with sodium hydrogen carbonate, and extracted forty or fifty times with hot amyl alcohol. The base extracted in this way was removed from its amyl alcoholic solution by dilute hydrochloric acid, and the acid solution evaporated to a small bulk. When sufficiently concentrated, radiating clusters of long, silky needles commenced to separate out, in the form characteristic of morphine hydrochloride, and their identity with this salt was proved by a determination of the water of crystallisation.

0.9322 at  $120^{\circ}$  lost 0.1322  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 14.1$ .

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HCl}\cdot 3\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 14.3$  per cent.

A bye-product therefore appears to be formed, which, on heating with water, is readily reconverted into morphine. This product has not yet been isolated. No trace of isomorphine could be detected.

*Acetylchloromorphide*,  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{NCl}\cdot\text{CO}\cdot\text{CH}_3$ , can be prepared from chloromorphide by means of either acetic anhydride or acetyl chloride, the better result being obtained by the use of the latter. Chloromorphide, mixed with about five times its weight of acetyl chloride, was heated for four or five hours on a water-bath in a reflux apparatus. The base nearly all dissolved. At the end of the reaction, the excess of acetyl chloride was distilled off, the residue dissolved in water, sodium carbonate added, and the base extracted with ether. On distilling off the ether, the acetyl derivative remained behind, and was purified by recrystallising two or three times from absolute alcohol and finally from acetone.

Acetylchloromorphide forms small, white, glistening plates, which soften at  $173^{\circ}$ , and melt at  $174$ — $178^{\circ}$ , several recrystallisations being required before a specimen can be obtained melting at the higher temperature.

0.1545 gave 0.3813  $\text{CO}_2$  and 0.0880  $\text{H}_2\text{O}$ .  $\text{C} = 67.31$ ;  $\text{H} = 6.32$ .

0.1562 „ 0.3849  $\text{CO}_2$  „ 0.0830  $\text{H}_2\text{O}$ .  $\text{C} = 67.20$ ;  $\text{H} = 5.90$ .

0.2338 „ by Carius' method, 0.0923  $\text{AgCl}$ .  $\text{Cl} = 9.76$ .

$\text{C}_{19}\text{H}_{20}\text{O}_3\text{NCl}$  requires  $\text{C} = 66.00$ ;  $\text{H} = 5.78$ ;  $\text{Cl} = 10.27$  per cent.

Although this substance was repeatedly crystallised, a pure specimen could not be obtained.

From the mother liquors, a very small amount of crystalline substance was obtained melting at  $137-145^\circ$ . The quantity was not sufficient for further investigation.

The *hydrochloride* was made by grinding up the base with 10 per cent. hydrochloric acid. It was recrystallised from water, from which it separated in silky needles, but by this means only 1.2 grams of salt were obtained from 5 grams of the base. As the mother liquors from this product decomposed on concentrating, becoming strongly acid, water was evidently an unsatisfactory solvent for recrystallisation. When administered *per os*, this salt produced no narcotic effects.

#### BROMOMORPHIDE.

Phosphorus tribromide acts on dry morphine with such violence that the mixture spontaneously takes fire. For this reason, the tribromide must be diluted with some inactive solvent to obtain a satisfactory result.

Twenty grams of morphine, previously dried at  $120^\circ$ , are thrown into a solution of 20 grams of phosphorus tribromide in 80 grams of chloroform, and the whole heated for four or five hours on a water-bath in a reflux apparatus. At the end of this time, a yellow, pasty mass is formed underneath the chloroform. This is disintegrated with alcohol, of which a quantity about equal in bulk to the chloroform is added. The whole is stirred round and warmed, until a not quite clear, homogeneous solution is obtained. This is then filtered, and the precipitate, consisting of a little yellow phosphorus mixed with hydrobromide of the base, is washed well with hot water, the washings being added to the filtrate, which is finally mixed with about twice its volume of water. The chloroform then separates out. The whole is then added in small quantities at a time, in a separating funnel, to a solution of excess of sodium carbonate over which a layer of ether stands, and the mixture vigorously shaken after each addition. The base is thus set free from the solution of its hydrobromide, and extracted with the mixture of chloroform and ether. Great care must be taken to prevent the base separating in pasty lumps, for these are not readily soluble in the chloroform-ether mixture; if formed, they must be redissolved in acid, the base regenerated from this, and extracted as just described. Bromomorphide is readily soluble in chloroform, but on concentrating the solution in this solvent, a hard,



porcelain-like mass is obtained, consisting of a mixture of the base with chloroform, from which the chloroform can only be expelled with great difficulty. On the other hand, the base is too slightly soluble in ether for it to be advisable to use this solvent alone. Satisfactory results, however, are obtained by the employment of the ether-chloroform mixture. After extracting four times with a mixture of chloroform and ether, very little of the base remains in the aqueous mother liquors. The chloroform-ether extract is then washed four or five times with water to extract the alcohol, rapidly dried with calcium chloride, filtered, and distilled. The base remains behind as a porcelain-like mass with a certain amount of chloroform adhering. On warming for some time on a water-bath with alcohol and then evaporating, a thick syrup is obtained, which is free from chloroform, and solidifies on standing for a short time to a hard mass, which can be readily powdered in a mortar. After drying the powder thus obtained in a water oven, it is further purified by recrystallisation. About 20 grams of base in this crude form are obtained from 20 grams of morphine.

In order to purify the product, the only convenient solvent available is ether. As, however, it is only slightly soluble in this liquid, it is placed in a Soxhlet apparatus, and extracted for several hours with pure dry ether. It then separates from the ether in hard masses of minute crystals, which are collected, and are quite pure enough for most purposes. A further amount of the base is obtained by concentration of the ethereal-mother liquor. For analysis the substance was recrystallised from ether two or three times. After the first ethereal extraction a certain amount of product remains undissolved. This has not yet been further investigated. As a rule, about 45 grams of recrystallised base are obtained from 60 grams of crude product.

Bromomorphide forms a microcrystalline powder of intensely bitter, nauseous taste. It is readily soluble in alcohol or chloroform, but only slightly so in pure dry ether. From benzene or ethyl acetate it separates in a gelatinous form, resembling that obtained from chloroform. It melts at 169—170°.

0.1692 gave 0.3694 CO<sub>2</sub> and 0.0841 H<sub>2</sub>O. C=59.5; H=5.52.

0.1227 „ 0.2677 CO<sub>2</sub> „ 0.0622 H<sub>2</sub>O. C=59.5; H=5.63.

0.5030 „ 18.8 c.c. moist nitrogen at 21° and 763 mm. N=4.27.

0.3620 „ 0.1904 AgBr. Br=22.38.

C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>NBr requires C=58.62; H=5.17; N=4.02; Br=23.00  
per cent.

A determination of the specific rotation in methyl alcohol gave the following result:

$$[\alpha]_D = +1^{\circ}52', l=1 \text{ dcm.}, c=2.837, [\alpha]_D^{25} = +65.9^{\circ}.$$

Bromomorphide is also obtained when morphine is mixed with four or five times its weight of 45 per cent. hydrobromic acid solution, and the whole heated for 2 or 3 minutes over a free flame, until the mixture begins to darken in colour. The product is then made alkaline with sodium carbonate, and the base extracted with an ether-chloroform mixture. A little unchanged morphine remains undissolved. For preparing large quantities of bromomorphide, the phosphorus tribromide method is the more convenient.

The salts of bromomorphide are much more stable than those of the corresponding chloro-compound, and for this reason can be recrystallised from water with very little loss. They are made by grinding up the base with a slight excess of acid. The *hydrochloride* crystallises from water in glistening needles containing  $1\text{H}_2\text{O}$ .

0.4545, at  $115^\circ$ , lost  $0.0188 \text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 4.14$ .

$\text{C}_{17}\text{H}_{18}\text{O}_2\text{NBr} \cdot \text{HCl} \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 4.47$  per cent.

0.3646 air-dried substance gave 0.3022 mixed  $\text{AgCl}$  and  $\text{AgBr}$ .

$\text{AgCl} + \text{AgBr}$  calc. = 0.3 gram.

For the determination of the specific rotation, the anhydrous salt obtained by recrystallisation from alcohol was employed.

$\alpha_D = +1.17'$ ;  $l = 1 \text{ dcm.}$ ;  $c = 3.157$ ;  $[\alpha]_D^{25} = +41.1^\circ$ .

The *hydrobromide* is very similar in appearance to the hydrochloride.

0.7492, at  $120^\circ$ , lost  $0.0355 \text{H}_2\text{O}$ . \*  $\text{H}_2\text{O} = 4.73$ .

0.2720 air-dried substance gave 0.2242  $\text{AgBr}$ .  $\text{Br} = 35.07$ .

$\text{C}_{17}\text{H}_{18}\text{O}_2\text{NBr} \cdot \text{HBr} \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 4.03$ ;  $\text{Br} = 35.77$  per cent.

For the determination of the specific rotation a specimen recrystallised from alcohol was employed:

$\alpha_D = +1.0'$ ;  $l = 1 \text{ dcm.}$ ;  $c = 2.53$ ;  $[\alpha]_D^{25} = +39.5$ .

#### DEOXYMORPHINE

Chloromorphide was suspended in about five times its weight of concentrated hydrochloric acid, excess of granulated tin added to the mixture, and the whole heated for 2 or 3 hours on a water-bath. A thick syrup separated out after a time. The liquid was poured off from the undissolved tin, which was then washed several times with hot water to dissolve out all the separated syrup. After filtration, the liquid was saturated with hydrogen sulphide whilst still warm, then corked up, and allowed to stand for some time. The precipitated stannous sulphide is subsequently filtered off and washed with hot water, the washings being added to the filtrate, which is then concen-

trated. On decomposition takes place at  $120^\circ$ , the substance becoming somewhat

trated over a free flame, under diminished pressure. If not concentrated too far, crystals of the new hydrochloride will separate out, and these, after filtering off and recrystallising once or twice from hot water, are quite pure. If, however, the new hydrochloride separates as an oil, it is advisable to neutralise carefully the strongly acid liquid with caustic soda and evaporate to dryness in a vacuum. The product thus obtained is then ground up to a fine powder, and extracted with absolute alcohol to separate the hydrochloride of the base from the inorganic salts with which it is mixed. On evaporation of the alcoholic extract, a syrup is obtained, which partly solidifies on mixing with water. The solid part can then be collected and recrystallised from water. Owing to the large amount of uncrystallisable matter, the yield of this hydrochloride was very small, and various attempts were made to increase the amount, but without success. As the product could not be obtained in large quantities, it was not subjected to a detailed investigation.

The hydrochloride separates from water in glistening needles containing  $1\frac{1}{2}\text{H}_2\text{O}$ . The base is soluble in ether, but has not yet been investigated.

0.8050, at  $120^\circ$ , lost 0.0665  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}=8.25$ .

0.1196 gave 0.2707  $\text{CO}_2$  and 0.0748  $\text{H}_2\text{O}$ .  $\text{C}=61.66$ ;  $\text{H}=6.94$ .

0.3592 „ 12.8 c.c. moist nitrogen at  $19^\circ$  and 755 mm.  $\text{N}=4.06$ .

0.3135\* „ 0.1333  $\text{AgCl}$ .  $\text{Cl}=10.52$ .

$\text{C}_{17}\text{H}_{19}\text{O}_2\text{N} \cdot \text{HCl} \cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{C}=61.35$ ;  $\text{H}=6.91$ ;  $\text{N}=4.21$ ;  
 $\text{Cl}=10.7$ ;  $\text{H}_2\text{O}=8.12$  per cent.

The specific rotation was determined with a specimen recrystallised from water:

$\alpha_D = +3.19'$ ;  $l=1$  dm.;  $c=2.363$ ;  $[\alpha]_D^{20} = +140.3^\circ$ .

#### ISOMORPHINE.

Isomorphine is most conveniently prepared from bromomorphide. For this purpose, 15 grams of bromomorphide are heated in a reflux apparatus with 150 c.c. of water; care being taken that the suspended base is not superheated, the flask, on this account, being repeatedly shaken. After about 1 hour the whole of the bromomorphide disappears, and a clear, light brown liquid is formed, which can be partly decolorised by boiling with animal charcoal. After filtering from the animal charcoal, the liquid is concentrated to a syrupy consistence. On stirring, the syrup partly solidifies to a thick, crystalline paste. The crystals are then separated from the mother liquors, washed

\* This analysis was done by Carius' method, in order to be sure that there was no chlorine in the substance other than that in the acid.

with a little alcohol, and spread on a porous plate. They are already nearly white; owing to their extreme solubility in water, purification is best effected by dissolving them in a large quantity of hot alcohol, and concentrating the solution until the hydrobromide separates out as a crystalline powder.

The *hydrobromide* crystallises from water, with  $1\text{H}_2\text{O}$ , in hard, stumpy prisms.

0.7078, at  $110-120^\circ$ , lost  $0.0360\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 5.08$ .

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HBr}\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 4.69$  per cent.

It separates from alcohol as a granular, crystalline powder, without water of crystallisation.

0.2161 gave  $0.4466\text{CO}_2$  and  $0.1058\text{H}_2\text{O}$ .  $\text{C} = 56.36$ ;  $\text{H} = 5.40$ .

0.1688 „  $0.3470\text{CO}_2$  „  $0.0840\text{H}_2\text{O}$ .  $\text{C} = 56.06$ ;  $\text{H} = 5.50$ .

0.2817 „  $0.1433\text{AgBr}$ .  $\text{Br} = 21.64$ .

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HBr}$  requires  $\text{C} = 55.75$ ;  $\text{H} = 5.46$ ;  $\text{Br} = 21.85$  per cent.

A determination of the specific rotation gave the following result:

$$\alpha_D = -3^\circ 10'; l = 1 \text{ dm.}; c = 2.49; [\alpha]_D^{18} = -127.2^\circ.$$

The corresponding salt of morphine crystallises with  $2\text{H}_2\text{O}$ , and when recrystallised from alcohol in the anhydrous form gave for the specific rotation the following result:

$$\alpha_D = -5^\circ; l = 2 \text{ dm.}; c = 2.49; [\alpha]_D^{18} = -100.4^\circ.$$

In order to obtain salts other than the hydrobromide, the solution of the latter, obtained by decomposition of bromomorphide, is concentrated, made alkaline with sodium carbonate, and extracted five or six times with hot amyl alcohol. To prepare the hydrochloride, the amyl alcoholic solution is extracted with dilute hydrochloric acid, and the acid solution evaporated to a syrup and left to crystallise.

The *hydrochloride* is excessively soluble in water, from which it separates in beautiful, transparent, anhydrous, regular octahedra. The specimen analysed was recrystallised from a large quantity of absolute alcohol, in which it is only slightly soluble.

0.2913 required  $9.2 \text{ c.c. } N/10 \text{ AgNO}_3$ .  $\text{Cl} = 11.21$ .

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HCl}$  requires  $\text{Cl} = 11.04$  per cent.

A determination of the specific rotation gave the following result:

$$\alpha_D = -7^\circ 9'; l = 1 \text{ dm.}, c = 4.76, [\alpha]_D^{20} = -150^\circ.$$

The corresponding morphine salt crystallises from water in masses of silky, radiating needles containing  $3\text{H}_2\text{O}$ , and is soluble in 20 times its weight of water. For purposes of comparison, a

specimen, free from water of crystallisation, was prepared by recrystallising from alcohol, and gave the following result :

$$\alpha_D = -2^\circ 30', l = 1 \text{ dm.}, c = 2.240, [\alpha]_D^{25} = -111.5^\circ.$$

The *sulphate* was prepared by treating the hydrochloride with a solution of silver sulphate and evaporating the filtrate very nearly to dryness. It is excessively soluble in water, but insoluble in alcohol, and could not therefore be recrystallised. For this reason, its properties were not accurately determined, but it differs very markedly from the neutral sulphate of morphine.

*Isomorphine* was originally prepared by treating a concentrated solution of the hydrobromide with aqueous ammonia in the presence of ether; the freshly precipitated base is dissolved by the ether, from which, however, it rapidly separates again in a beautiful, crystalline form. Only a portion of the base could be obtained in this way, even after 15 or 20 extractions with ether. The rest remained in the alkaline liquid, and on evaporating the latter to dryness in a vacuum, a mixture of the hydrobromide with ammonium bromide was obtained. The base is best obtained, however, by decomposing the hydrochloride by sodium methoxide in methyl alcohol. Sodium chloride is precipitated, and after filtration the nearly pure base is obtained from the mother liquor.

Isomorphine is free from any bitter taste. It dissolves in large quantities of ethyl alcohol, is readily soluble in methyl alcohol, but not very readily so in most other organic reagents, and can best be recrystallised from a mixture of methyl alcohol and ethyl acetate, from which it separates in the form of small, white, glistening needles melting at  $246-248^\circ$ . It is also soluble in, and can be recrystallised from, hot water.

0.1638 gave  $0.4320 \text{ CO}_2$  and  $0.1004 \text{ H}_2\text{O}$ .  $C = 71.92$ ;  $H = 6.81$ .

0.2690 „ 11.8 c.c. moist nitrogen at  $24^\circ$  and 757 mm.  $N = 4.90$ .

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$  requires  $C = 71.6$ ;  $H = 6.66$ ;  $N = 4.91$  per cent.

A determination of the specific rotation was made with a solution of the base in methyl alcohol, and gave the following result :

$$\alpha_D = -3^\circ 17', l = 1 \text{ dm.}, c = 2.01, [\alpha]_D^{25} = -164.3^\circ.$$

Morphine\* is similar to isomorphine in many respects, and melts at  $254^\circ$ . A specimen, recrystallised from methyl alcohol, from which it separates in beautiful groups of radiating crystals, gave the following

\* It does not seem to be generally known that morphine can be readily recrystallised from various solvents, especially methyl alcohol, in which it is quite readily soluble.

numbers when its specific rotation in methyl alcoholic solution was determined.

$$\alpha_D = -3^{\circ}0', l=1 \text{ dm.}, c=2.292, [\alpha]_D^{25} = -130.9^{\circ}.$$

The colour reactions of isomorphine are similar to those of morphine.

*Isomorphine Methiodide.*—4.2 grams of isomorphine and 5 grams of methyl iodide were dissolved in 150 c.c. of methyl alcohol and the mixture boiled on a water-bath. After about 20 minutes, the methiodide commenced to separate. The boiling was continued for 1 hour, at the end of which time the crystals of the methiodide were filtered off. A further small quantity was obtained from the mother liquors. After drying at  $80^{\circ}$ , the substance was found to melt with some decomposition at  $276^{\circ}$ . It is soluble in hot water, from which it separates on cooling in the form of white, glistening needles. It dissolves readily in 25 per cent. caustic soda solution.

0.3980 required 9.35 c.c.  $N/10$   $\text{AgNO}_3$  solution.  $I=30.0$ .

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}, \text{CH}_3\text{I}$  requires  $I=30.6$  per cent.

A determination of the specific rotation in water gave the following results:

$$\alpha_D = -1^{\circ}38', l=1 \text{ dm.}, c=1.696, [\alpha]_D^{25} = -91.5^{\circ}.$$

Morphine methiodide melts at nearly the same temperature as the isomorphine derivative. A determination of its specific rotation in water gave the following result:

$$\alpha_D = -0^{\circ}51', l=1 \text{ dm.}, c=1.162, [\alpha]_D^{25} = -72.9^{\circ}.$$

*Action of Acetic Anhydride on Isomorphine Methiodide.*—Four grams of isomorphine methiodide were suspended in 40 grams of acetic anhydride, to this was added  $\frac{1}{2}$  gram fused sodium acetate, and the whole boiled on a sand-bath until solution was effected, when 1.6 grams of silver acetate (1 mol.) were introduced. Immediate precipitation of silver iodide occurred, and the mixture was boiled in an oil-bath for 6 hours. Silver iodide was then filtered off, and the filtrate heated in a sealed tube for 3 hours at  $180^{\circ}$ . The acetic anhydride was then distilled off at  $170^{\circ}$  in an oil-bath, and the concentrated, light brown solution poured into twice its volume of water. A small quantity of a brown oil separated, which quickly solidified, and was collected, powdered, and dried. The crude substance only amounted to 0.3 gram. This was dissolved in glacial acetic acid, the solution boiled with animal charcoal, and filtered. On cooling, the filtrate deposited small, glistening needles, which were collected and found to melt at  $154$ — $155^{\circ}$ . They were then recrystallised from a large quantity of dry ether, from which they separated in small, white needles melting at  $153.5^{\circ}$ . O. Fischer and Vongerichten obtained an acetyl di-

hydroxyphenanthrene from morphine methiodide which melted at  $159^{\circ}$  (*Ber.*, 1886, 19, 792). The filtrate from the solid product, which contains the main product of the action of acetic anhydride and silver acetate on morphine methiodide, when made alkaline, deposits a base which has not yet been investigated.

*Further reactions of Isomorphine Methiodide.*—2.1 grams of isomorphine methiodide were dissolved in hot water, and to this an aqueous solution of 0.78 gram of silver sulphate was added. The precipitated silver iodide was filtered off, and to the filtrate an aqueous solution of 0.8 gram of crystallised barium hydroxide was added, and the whole boiled. Carbon dioxide was passed through for a short time to precipitate the very slight excess of baryta. After filtration from the precipitated barium sulphate, the strongly alkaline solution was evaporated to a syrup, which, when placed in a vacuum, deposited a mass of fern-like crystals. On further evaporation in a vacuum, the crystals dissolved, and a syrup was obtained which, on standing overnight, became a hard, solid mass. This, when powdered and dissolved in methyl alcohol, gave a strongly alkaline solution. Excess of methyl iodide was added, and the mixture allowed to stand for 2 days. At the end of this time, it was still strongly alkaline, and did not become neutral until boiled on a water-bath for 1 hour. The methyl alcohol, with excess of methyl iodide, was evaporated off, leaving a syrup which was dissolved in water, and the solution boiled with animal charcoal, filtered, evaporated on a water-bath to a syrup, and placed in a vacuum over sulphuric acid. The resulting varnish gradually became quite hard, and could be powdered; it was deliquescent, and almost insoluble in ethyl alcohol, but readily soluble in methyl alcohol or cold water. It did not agree in any of its properties with codeine methiodide.

0.3908 required 8.7 c.c.  $N/10$   $\text{AgNO}_3$ .  $I = 28.2$ .

$\text{C}_{17}\text{H}_{18}(\text{OCH}_3)_2\text{O}_2\text{N}, \text{CH}_3\text{I}$  requires  $I = 28.8$  per cent.

A determination of the specific rotation in water gave the following result:

$$\alpha = -2^{\circ}0', l = 1 \text{ dm.}, c = 2.074, [\alpha]_D^{25} = -96.4^{\circ}.$$

Preliminary experiments have been made for the preparation of the acetyl compound, and the results will be communicated in a later paper.

*Addendum.*—Since the communication of the above paper to the Society, Pschorr and Sumuleanu have published their synthesis of morphol (*Ber.*, 1900, 33, 1810), and confirmed the formula assigned to this substance by Vongerichten.

XCII.—*The Oxime of Mesoxamide and some Allied Compounds.*

By MARTHA ANNIE WHITELEY, B.Sc.

By the action of nitrosyl chloride on malonamide a substance is obtained which is characterised by the intense violet coloration it gives when mixed with ferrous sulphate and an alkali (Tilden and Forster, *Trans.*, 1895, 67, 490).

This substance can be prepared by the action of liquid nitrosyl chloride on malonamide in sealed tubes at the ordinary temperature. After several days there is evidence of considerable pressure, for, on opening the tubes, hydrogen chloride escapes together with unchanged nitrosyl chloride. It was more conveniently prepared, however, by passing a current of gaseous nitrosyl chloride through chloroform in which malonamide was suspended. The gas was rapidly absorbed, but the amide was attacked very slowly at the ordinary temperature, and it was necessary to warm the liquid from time to time to about 45–50°; a brisk evolution of gas then occurred, and the liquid became colourless. The white, crystalline powder was filtered off, washed with chloroform, and spread on a clock glass to dry; it continued to evolve hydrogen chloride for some time.

The crude product thus obtained was readily soluble in water, and the concentrated solution decomposed with evolution of carbon dioxide when evaporated on a steam-bath. The aqueous solution was therefore allowed to evaporate in a vacuum over sulphuric acid, and the dry residue extracted repeatedly with boiling ethyl acetate. A small quantity of insoluble matter was left, which was found to be ammonium chloride. From the ethyl acetate solution, a white, crystalline powder was deposited, which gave very strongly the characteristic colour reaction with ferrous sulphate. After recrystallisation from ethyl acetate, the substance melted with decomposition at 187°. It is readily soluble in water or alcohol, forming acid solutions from which, by spontaneous evaporation, it crystallises in small, clear prisms. It is also soluble in boiling acetone, ethyl acetate, or acetic acid, crystallising from the last in well-developed prisms containing acetic acid, which is given up on exposure to the air, the crystals efflorescing. It is insoluble in benzene, ether, or light petroleum. The aqueous solution assumes a bright yellow colour on the addition of ammonia, soda, or potash. The substance contains no chlorine. After boiling with hydrochloric acid, it reduces Fehling's solution. It does not give Liebermann's test. On analysis:



0.0919 gave 26 c.c. moist nitrogen at  $20.5^{\circ}$  and 766.7 mm.  $N = 32.58$ .

0.0766 " 21.5 c.c. " " "  $20^{\circ}$  " 768 mm.  $N = 32.45$ .

$C_5H_5O_3N_3$  requires  $N = 32.06$  per cent.

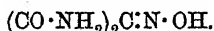
In a molecular weight determination :

0.0981 in 23.93 acetic acid gave a depression  $0.135^{\circ}$ . Mol. wt. = 118.4.

0.1351 in 23.93 " " " "  $0.187^{\circ}$ . Mol. wt. = 117.7.

The molecular weight of  $C_5H_5O_3N_3$  is 131.

The substance is therefore an oxime having the formula



*Acetyl Derivative*,  $(CO \cdot NH_2)_2C:N \cdot O \cdot CO \cdot CH_3$ .—The oxime dissolved in acetic anhydride on warming, and from the solution bright, well-formed, prismatic crystals separated; these were filtered off, washed with acetic anhydride, and dried in a desiccator. The acetyl derivative melts, with decomposition, at  $190^{\circ}$ , and dissolves sparingly in cold, but readily in hot water, doubtless suffering hydrolysis, as the solution is coloured yellow by an alkali, and gives the characteristic violet coloration on the addition of ferrous sulphate. On analysis :

0.1473 gave 30.5 c.c. moist nitrogen at  $17^{\circ}$  and 767.65 mm.  $N = 24.28$ .

$C_5H_7O_4N_3$  requires  $N = 24.28$  per cent.

*Salts*.—The acid character of the oxime is strongly marked. One hydrogen atom is readily replaced by metals, giving rise to salts which, with one or two exceptions, are of a bright yellow colour. The alkali salts are readily soluble in water, and are precipitated in the form of silky, yellow needles on the addition of alcohol to the solutions. The silver, lead, barium, and calcium salts are less soluble, and separate in a crystalline form from concentrated solutions.

The *silver* salt,  $(CO \cdot NH_2)_2C:N \cdot OAg$ , was analysed, with the following result :

0.1650, on ignition, gave 0.0744 Ag.  $Ag = 45.09$ .

$C_5H_4O_3N_3Ag$  requires  $Ag = 45.34$  per cent.

The *potassium* salt,  $(CO \cdot NH_2)_2C:N \cdot OK$ , was prepared by adding excess of potash to the concentrated aqueous solution of the oxime, and precipitating the salt by the addition of alcohol, filtering, and washing with alcohol until free from alkali.

0.5652 gave 0.2905  $K_2SO_4$ .  $K = 23.08$ .

$C_5H_4O_3N_3K$  requires  $K = 23.12$  per cent.

*Ferrous Potassium Salt*,  $(CO \cdot NH_2)_2C:N \cdot OK, [(CO \cdot NH_2)_2C:N \cdot O]_2Fe$ .—The capacity of forming coloured salts is certainly the most striking property of the oxime. The characteristic violet coloration with

ferrous sulphate and an alkali is due to the formation of a double salt, which is obtained in the form of small, well-defined prisms of a purple colour, with a green or bronze lustre when ferrous sulphate is added to a concentrated aqueous solution of the potassium, sodium, ammonium, barium, or calcium salt. For the purpose of analysis, the ferrous potassium salt was prepared by adding freshly made ferrous sulphate solution to a concentrated aqueous solution of the potassium salt, the crystalline precipitate being rapidly filtered, washed two or three times with cold water, in which it was very soluble, and dried in a desiccator. When dry, the salt is perfectly stable, but is rapidly decolorised when left exposed in the damp state.

0.1351 gave 0.0223  $\text{Fe}_2\text{O}_3$ .  $\text{Fe} = 11.56$ .

0.4546 „ 0.0732  $\text{Fe}_2\text{O}_3$  and 0.0787  $\text{K}_2\text{SO}_4$ .  $\text{Fe} = 11.27$ ;  $\text{K} = 7.77$ .

$(\text{C}_5\text{H}_4\text{O}_3\text{N})_3\text{KFe}$  requires  $\text{Fe} = 11.54$ ;  $\text{K} = 8.06$  per cent.

The *ethyl* derivative,  $(\text{CO}\cdot\text{NH}_2)_2\text{C}\cdot\text{N}\cdot\text{OEt}$ , could not be obtained by the action of ethyl iodide and sodium ethoxide on the oxime. It was prepared, however, by the action of ethyl iodide on the silver salt suspended in alcohol; the change took place readily on warming, silver iodide being precipitated and a yellow solution formed, which, after filtration, was evaporated to dryness, and the yellow, crystalline residue recrystallised from boiling ethyl acetate. The derivative was thus obtained in the form of minute, colourless octahedra melting at  $150-151^\circ$ . It dissolves readily in water, but suffers hydrolysis as the solution becomes yellow with alkalis, changing to violet on the addition of ferrous sulphate.

0.1092 gave 25.7 c.c. moist nitrogen at  $20^\circ$  and 769.1 mm.  $\text{N} = 27.28$ .

$\text{C}_5\text{H}_3\text{O}_3\text{N}_3$  requires  $\text{N} = 26.41$  per cent.

Analyses of the oxime and certain of its metallic and alkyl derivatives having indicated that it is the isonitroso-derivative of malonamide, it was prepared by three other methods, which confirm this view of its constitution—namely, by the action of nitrous acid on malonamide, by the action of hydroxylamine on dibromomalonamide, and by the action of ammonia on ethyl isonitrosomalonate.

*Action of Nitrous Acid on Malonamide.*—The gases obtained by the action of nitric acid of sp. gr. 1.3 on white arsenic were passed into a supersaturated solution of malonamide kept cool by ice. When the precipitated malonamide had all passed into solution and the liquid had acquired a blue or green colour, the tube was gently warmed until evolution of nitrous fumes ceased and the solution was colourless; it was then cooled and the operation repeated. Finally, the solution was allowed to evaporate in a vacuum over sulphuric acid, and the hard, crystalline masses thus obtained were dried, ground to powder, and

recrystallised from ethyl acetate. By this method, a yield of 40 per cent. of the theoretical was readily obtained.

*Action of Hydroxylamine on Dibromomalonamide.*—Dibromomalonamide, prepared by the action of bromine on malonamide (Freund, *Ber.*, 1884, 17, 782), was suspended in an alkaline solution of hydroxylamine hydrochloride ( $1\frac{1}{2}$  mols.) and warmed on the steam-bath for 48 hours. At the end of that time, all the dibromomalonamide had passed into solution, the liquid had a bright yellow colour, and one drop gave, with ferrous sulphate, an intense violet colour, indicating the presence of the oxime in considerable quantity. The compound was not isolated, however, owing to the difficulty of separating it from the mixture of sodium bromide and chloride.

*Action of Ammonia on Ethyl Isonitrosomalonnate.*—When ethyl isonitrosomalonnate was mixed with excess of ammonia solution of sp. gr. 0.925, heat was developed and a dark yellow solution formed. After standing for sixteen hours, the yellow crystalline deposit was removed by filtration, washed with alcohol, and dried. It was identified as the ammonium salt of the oxime of mesoxamide by its colour, crystalline form, solubility, and the formation of the dark violet crystals of the double salt on treatment with ferrous sulphate solution. The yield was 80 per cent. of the theoretical.

*Action of Nitrous Acid on the Oxime.*—In preparing the oxime by the action of nitrous acid on malonamide, it was noticed that a white precipitate of long, silky needles was frequently deposited in the rapidly cooled solution. This is a product of the action of nitrous acid on the oxime, for it can be prepared by adding an aqueous solution of nitrous acid to the oxime, or to its potassium salt rendered colourless by a drop of hydrochloric acid. The substance was separated by filtration, washed with water and alcohol, and dried in a desiccator. It melts with decomposition at  $215-220^{\circ}$ , is slightly soluble in cold, but readily soluble in boiling water, and dissolves readily in alkalis, forming pale yellow solutions from which it is reprecipitated in the crystalline form on the addition of hydrochloric acid. The alkaline solutions do not give a violet coloration with ferrous sulphate. After boiling with hydrochloric acid, the substance does not reduce Fehling's solution; hence it is not an oxime. For the purpose of analysis, a specimen was recrystallised from boiling water, washed with cold water and with alcohol, and dried in a desiccator.

0.094 gave 26.6 c.c. moist nitrogen at  $21.5^{\circ}$  and 750.8 mm.  $N = 31.75$  per cent.

By heating the substance with caustic potash, and collecting the distillate in a known quantity of sulphuric acid, 0.4213 evolved ammonia equivalent to 0.2088  $H_2SO_4$ .  $N$  as  $NH_3 = 14.17$  per cent.

These results agree with the numbers calculated from the formula of a pseudonitrole,  $(\text{CO}\cdot\text{NH}_2)_2\text{C}(\text{NO})\cdot\text{NO}_2$ , which requires 31.82 per cent. of nitrogen and 15.91 per cent. of nitrogen as amidogen. It does not, however, possess the properties usually regarded as characteristic of a pseudonitrole, and it does not respond to Liebermann's test.

The substance appears to be dimorphous, crystallising in long, silky needles, or very bright, shining plates, according to the conditions; the former are thrown down from the mixture when it is rapidly cooled, the shining plates are deposited when the cooling is gradual. Moreover, the needles tend to pass into the other form on recrystallising from water, or on long standing in the mixture.

By the further action of nitrous acid on malonamide, ammonium quadroxalate and oxalic acid are formed and constitute the only solid products.

*Reduction of the Oxime.*—The oxime was readily reduced by the action of hydriodic acid on a concentrated aqueous solution in the cold. The liberated iodine was removed by shaking with mercury, and the excess of hydriodic acid by mercuric oxide. After removal of a trace of mercury from the solution by means of hydrogen sulphide, the liquid was evaporated to dryness, taken up with a little water, alcohol added until it produced turbidity, and the solution rendered clear by warming. Large, prismatic crystals associated with the cubical crystals of ammonium iodide were slowly deposited from the solution. The prismatic crystals, which consisted of the hydriodide of a base, blackened, but did not melt at  $250^\circ$ . On analysis:

0.1981 gave 0.1881 AgI.  $\text{I} = 51.30$ .

$\text{C}_8\text{H}_8\text{O}_2\text{N}_3\text{I}$  requires  $\text{I} = 51.78$  per cent.

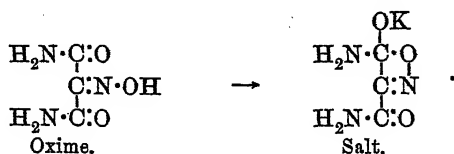
The reduction product of the oxime is therefore *aminomalonalamide*,  $(\text{CO}\cdot\text{NH}_2)_2\cdot\text{CH}\cdot\text{NH}_2$ , but the supply of material was too small to allow of the isolation of the base.

The capacity of forming red or purple alkali salts, and deep blue or violet ferrous salts, is characteristic of violuric acid, dimethylvioluric acid, isonitrosomalonylguanidine, and other ring compounds which contain the grouping  $\text{OH}\cdot\text{N}:\text{C} \begin{smallmatrix} \text{CO}\cdot\text{N}: \\ \text{CO}\cdot\text{N}: \end{smallmatrix}$ .

According to Hantzsch (*Ber.*, 1899, 32, 594), the salts of violuric acid possess a constitution different from that of the acid, and involving transference of the hydroxyl from the oximido-group to the carbon atom of the adjacent carbonyl, and the subsequent linking of the nitrogen and the oxygen to form a four-membered ring.

The oxime of mesoxamide, although an open chain compound, also

contains the characteristic grouping  $\text{OH}\cdot\text{N}:\text{C} \begin{cases} \text{CO}\cdot\text{N}: \\ \text{CO}\cdot\text{N}: \end{cases}$ , and its formation of coloured salts may be due to a similar tautomeric change.



The only other substance which I have been able to find, having the property of giving a colour reaction with ferrous sulphate and an alkali, is isonitrosoguanidine, described by Thiele (*Annalen*, 1893, 273, 133). It was at first thought that there might be some resemblance between this compound and those to which reference has just been made, and some isonitrosoguanidine was therefore prepared for purposes of comparison. Investigation showed, however, that the colour produced by alkalis does not differ markedly from that of the compound itself, whilst the shade obtained with ferrous sulphate is bluish-red and quite distinct from that produced with the oxime of mesoxamide. The constitution assigned by Thiele to isonitrosoguanidine seemed to exclude from consideration the possibility of its being the analogue of these oximes, but to put the question to the test of experiment the oxime of mesoxamethylamide (isonitrosomalonomethylamide),  $\text{OH}\cdot\text{N}:\text{C}(\text{CO}\cdot\text{NHMe})_2$ , has been prepared by Andreasch's method (*Monatsh.*, 1895, 16, 773). Contrary to Andreasch's experience, I find that the barium salt of this oxime is distinctly yellow. On the addition of ferrous sulphate to a solution of an alkali salt of this compound, a violet colour was obtained indistinguishable from that produced with the oxime of mesoxamide.

Further experiments are in progress to ascertain to what extent the colour reaction with ferrous sulphate is modified by the substitution of other radicles for the aminic hydrogen atoms in the oxime of mesoxamide.

The oxime of pyruvamide differs in constitution from that of mesoxamide in containing a  $\text{CH}_3$  group in the place of one of the  $\cdot\text{CO}\cdot\text{NH}_2$  groups of the latter; it was therefore expected that it would give similar, although modified, colour reactions. It was prepared by the action of ammonia on ethyl oximidopyruvate, and is a colourless, crystalline substance which melts at  $176\text{--}177^\circ$ , and dissolves sparingly in cold, but readily in hot water. It was recrystallised from boiling ethyl acetate. On analysis:

0.0921 gave 22 c.c. moist nitrogen at  $20^\circ$  and 768.8 mm.  $\text{N} = 27.66$ .

$\text{C}_3\text{H}_6\text{O}_2\text{N}_2$  requires  $\text{N} = 27.45$  per cent.

Alkaline solutions of this oxime exhibit no decided yellow colour, and the precipitate formed on the addition of ferrous sulphate is pale red, darkening rapidly to a deep reddish-brown.

The oxime of pyruvamide is described by Hantzsch and Urbahn (*Ber.*, 1895, 28, 760) as melting at 174—175°, and prepared by the joint action of ammonia and hydroxylamine on ethyl pyruvate. Two attempts were made to prepare the compound according to the instructions given, but without success; the only product isolated was an extremely soluble substance, extracted by ether from the mixture. On distilling off the ether, a yellow, syrupy liquid was left, which eventually solidified into a mass of pale yellow, prismatic crystals covered with a thin layer of a transparent, yellow solid; the two were identical in properties, readily soluble in water, alcohol, ethyl acetate, or acetone, but less soluble in ether, and insoluble in benzene, light petroleum, or chloroform. The aqueous solution gave a deep cherry-red colour with ferric chloride, and a green precipitate with copper acetate; the faintly yellow solution formed with alkalis became reddish-brown on the addition of ferrous sulphate, and threw down a precipitate. For the purpose of analysis, the substance was recrystallised from ether; the colourless, crystalline powder thus obtained melted with decomposition at 143°. The nitrogen in each of the two specimens was estimated:

0.1006 gave 20.7 c.c. moist nitrogen at 20.5° and 764.9 mm. N = 23.65.

0.1096 „ 22.4 c.c. „ „ 21° „ 763.6 mm. N = 23.38.

$C_3H_6O_3N_2$  requires N = 23.73 per cent.

The compound is, therefore, the hydroxamic acid of oximidepropionic acid,  $CH_3 \cdot C(N \cdot OH) \cdot C \begin{smallmatrix} \nearrow N \cdot OH \\ \searrow OH \end{smallmatrix}$ .

All attempts to prepare an isonitroso-derivative from succinamide by the action of nitrosyl chloride or nitrous acid were unsuccessful. Succinamide suspended in chloroform is not attacked by nitrosyl chloride; when sealed in a tube with liquid nitrosyl chloride for 7 days, it was partly converted to succinic acid. It was completely converted to succinic acid when treated with nitrous acid in water solution.

This work was undertaken at the suggestion of Professor Tilden, to whom my thanks are due for much help and encouragement during its progress.

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XCIII.—*Phenylacetylchloramine and its Analogues.*

By HENRY E. ARMSTRONG.

BENDER, who was the first to show that the aminic hydrogen of acetanilide can be displaced by chlorine (*Ber.*, 1886, 19, 2272), effected the chlorination by adding a concentrated solution of bleaching powder to a concentrated aqueous solution of acetanilide mixed with an excess of acetic acid; as he refers to the interaction as one involving a slight rise of temperature, which makes it necessary to cool in warm weather, it is clear that he operated with cold solutions.

Several years ago, in the course of our experiments on the sulphonation of the chlor- and brom-anilines (*Proc.*, 1892, 8, 400), Mr. Briggs and I repeated Bender's experiments, but we were unsuccessful in obtaining the pure nitrogen chloride; it was always present in the product, but together with varying quantities of *p*-chloracetanilide. However, as it was easy, following Bender's directions, to convert the nitrogen chloride into its isomeride by digesting the crude product with concentrated muriatic acid, we adopted the method as being the simplest process in preparing large quantities of *p*-chloracetanilide; but we never succeeded in obtaining more than 60—70 per cent. of the amount to be expected.

Subsequently, at my request, two of my students, Messrs. Gidden and Spencer, carried out a series of experiments to discover the conditions under which Bender's compound was alone formed; and it was ascertained that almost the amount indicated by theory could be obtained by operating at an elevated temperature, but otherwise in accordance with his directions.

Five hundred grams of bleaching powder having been well stirred up with 3 litres of water, a solution of 300 grams of sodium carbonate in 1 litre of water was added, and the liquid was subsequently separated from the solid. A solution of 120 grams of acetanilide in 120 grams of glacial acetic acid having been poured into 6 litres of boiling water and the mixture well stirred, the whole of the clear solution of sodium hypochlorite, prepared as described, was at once added to the hot liquid, the temperature of which was about 80—85°. The solution immediately became turbid, and on stirring it well, the suspended matter clotted together and sank, leaving a clear, colourless liquid. An additional half-litre of hypochlorite solution was added to complete the precipitation. When the liquid was cold, the product was collected on a calico filter; in appearance, it resembled coarse sawdust, but the aggregates consisted of fine needles.

When the chlorination was effected at temperatures between about

0° and 50° in the manner described, the acetanilide being dissolved in sufficient glacial acetic acid to keep it in solution on pouring the liquid into water, the product was always a mixture of *p*-chloracetanilide with the nitrogen chloride, the proportion of the latter being less the lower the temperature. At the time, it was not easy to understand why such a paradoxical result was obtained, and especially why it was advantageous to operate at a high temperature. It should be added also that students who followed Messrs. Gidden and Spencer's directions were not always successful in imitating their results.

Slossen, in a paper published in 1895 (*Ber.*, 28, 3265), describes the preparation of phenylacetylchloramine and of the analogous formyl and benzoyl compounds by means of hypochlorous acid prepared by saturating an ice-cold 10 per cent. aqueous solution of sodium carbonate with chlorine and displacing the excess of the latter by a current of air. He succeeded in this way in completely converting acetanilide into the nitrogen chloride. Slossen's observations on the bromination of acetanilide are also noteworthy. He found that when acetic acid was used as a means of liberating hypobromous acid, only *p*-bromacetanilide was formed, but on using carbonic acid in place of acetic acid he was successful in obtaining the nitrogen bromide.

Recently, Chattaway and Orton have shown that Slossen's carbonic acid method is universally applicable, although without giving him the credit; and they do little more than mention Bender's work. Moreover, the description they give of the properties of the acetyl-nitrogen chloride and analogous compounds is in many respects very different from that given by Bender and Slossen; yet they make no reference to the fact that their results do not tally with those of previous observers, and in no way seek to justify their own statements.

According to Bender, phenylacetylchloramine may be recrystallised from very dilute acetic acid. When warmed with absolute alcohol, it dissolves, but after a short time the liquid boils violently and *p*-chloracetanilide begins to crystallise out. It may be boiled with water without undergoing change. Cold concentrated muriatic acid converts it into *p*-chloracetanilide, the interaction being a violent one. But according to Chattaway and Orton, although it dissolves readily in dilute acetic acid, long needles of *p*-chloracetanilide separate as the liquid cools; and in speaking of its preparation by Bender's method, they say: "The slightest excess of acetic acid causes the complete conversion of the substance into *p*-chloracetanilide," whilst in their account of the properties of the chloramines generally, they tell us that: "With alcohol the anilide is reformed." "With strong



hydrochloric acid, chlorine is set free and the anilide regenerated. . . . In some cases, however, under the influence of the acid, a portion of the compound undergoes an intramolecular transformation similar to that which takes place when it is heated."

Chattaway and Orton's statements are so entirely contrary to my own experience as well as to those of Bender and Slossen, that I have thought it to be necessary to look further into the matter, especially as this was desirable on other grounds.

Chattaway and Orton have advocated the view that when anilides are chlorinated or brominated, the nitrogen chloride or bromide is necessarily an intermediate product, and seem to claim originality for this explanation; they have forgotten to notice that in discussing the laws which govern substitution in benzenoid compounds thirteen years ago, I put forward this view, not only with reference to Bender's compound, but also in explanation of the production of ortho- and para-compounds generally, and that I have since often referred to it. In the synopsis of the discussion on laws of substitution which took place at the meeting of the British Institution at Dover in September last, which is printed in the report (pp. 683—687) after specifically referring to the conversion of phenylacetylchloramine into *p*-chloracetanilide, I said: "Moreover, bearing in mind the extreme readiness with which change takes place, for example, in the case of the formation of *p*-chloracetanilide from the compound  $\text{PhNAcCl}$ , or of sulphanilic from phenylsulphamic acid, it is difficult to believe that the formation of the one compound is not a necessary stage in the formation of the other: the readiness with which the substituted benzenoid compound is obtained is so great, that it is to be expected that both compounds would be formed together if they were independent products of the action of a single agent—just as, in fact, often happens in the case of para- and ortho-compounds." "It is very difficult to form any precise conception of the manner in which such 'isomeric changes' are brought about. Something more than a mere interchange of position of the radicles is involved in them: some agent intervenes; but the operation of the agent is easily overlooked, as only a minute quantity suffices in many cases, the action being 'fermentative' in character."

It was from this point of view, in the hope of discovering the catalyst by which the change is conditioned, that it appeared desirable to re-examine Bender's compound. I am much indebted to Messrs. P. V. Dupré and E. J. Fairhall for the assistance they have rendered me in the experiments.

From the outset, it was probable that hydrogen chloride was the

active catalyst; and there is little doubt that this is the case; it is at least certain that the compound is stable so long as the conditions are such as to preclude the presence of hydrogen chloride.

When prepared by Slossen's method, being produced practically in an alkaline medium, the crude product is alkaline, and it may be purified without difficulty by recrystallisation from a neutral solvent.

The carefully purified dry substance may be preserved in the dark for months unchanged. It may be recrystallised from acetic acid of any strength. When dissolved in alcohol, sooner or later, it usually undergoes isomeric change spontaneously, but it may be recrystallised from hot alcohol in the presence of a little acid sodium carbonate, or finely divided calcium carbonate; in fact, this appears to be by far the simplest method of effecting its purification. Yet, if a drop of muriatic acid be added to the warm alcoholic solution, the temperature at once begins to rise and the chloride is converted into *p*-chloracetanilide; the same change takes place when it is added to ordinary muriatic acid. In both cases, the action is very violent, if the quantity dealt with be at all considerable.

The properties of phenylacetyl bromamine appear to be very similar to those of the chloride; but it is far more sensitive to change. When it undergoes conversion into *p*-bromacetanilide in alcoholic solution, perhaps a small portion suffers reduction, but I am not satisfied that a sufficiently purified substance has been dealt with to decide this point.

*p*-Chlorophenylacetylchloramine, although reduced by concentrated muriatic acid in the manner indicated by Chattaway and Orton, appears to be to a large extent converted into dichloracetanilide when dissolved either in alcohol or in acetic acid and subjected to the action of a minute proportion of hydrogen chloride. It may be boiled with alkaline water without undergoing change, but if the liquid be then rendered faintly acid by adding muriatic acid and again heated, the isomeric change at once takes place.

The behaviour of dichlorophenylacetylchloramine is in accordance with Chattaway and Orton's statements, this compound being reduced both by alcohol and by muriatic acid without undergoing isomeric change.

The recognition of hydrogen chloride as being the catalytic agent which determines the isomeric change of the nitrogen chloride is of importance as defining the conditions under which compounds such as are under consideration must be prepared, and as affording an explanation of the special value of carbonic acid as the means of liberating hypochlorous acid.

The experiments made by Messrs. Gidden and Spencer above re-

ferred to, in which the complete conversion into nitrogen chloride was secured by operating at an elevated temperature, the amount of acetic acid used was relatively small in comparison with the amount of sodium carbonate, so that probably the chlorination was effected in the presence of acid carbonate; but in the unsuccessful experiments at lower temperatures, a relatively larger proportion of acetic acid was used, in order to maintain the acetanilide in solution; consequently, acetic acid was present in excess, and doubtless led to the liberation of sufficient hydrogen chloride to induce isomeric change.

Chattaway and Orton speak of phenylacetylchloramine as being "very easily and rapidly prepared by the action of bleaching powder on acetanilide suspended in excess of potassium bicarbonate solution." According to my experience, whatever excess of hypochlorite be taken, and however long the stirring be continued, the chlorination is almost always imperfect, and eventually at most 60—70 per cent. of *p*-chloracetanilide has been obtained. The difficulty is entirely got over by heating, and apparently the operation may be carried out on any scale. For example, a kilogram of acetanilide may be completely chlorinated within a few minutes in an ordinary housemaid's enamelled iron pail mounted on a gas burner and provided with an efficient stirrer. It is desirable to use both hypochlorite and acid carbonate in considerable excess; the acetanilide is quickly added to the concentrated solution containing these, and after vigorously stirring for a short time the temperature is raised to 50—60°.

In attempting to explain the manner in which the isomeric change is effected, it appears legitimate to assume that it is dependent on the combination of the chloramine with hydrogen chloride. A condition of extreme instability is thus engendered, and probably the first consequent change is one in which an atom of chlorine attached to the nitrogen atom escapes from the molecule together with an atom of hydrogen from the nucleus; a chlorine atom then slips into the nucleus in place of the latter, whilst the atom of hydrogen introduced in the molecule of hydrogen chloride takes the place of the chlorine atom of the chloramine, the ortho- or para-derivative being formed according to the conditions prevailing at the moment of change.

In justification of the view that hydrogen is withdrawn from the nucleus, attention may be directed to E. Fischer's observation that active aminoglutaric acid is racemised on benzoylation (*Ber.*, 1899, 32, 2464). This would seem to show that the chlorine of the benzoyl chloride is not removed in conjunction with aminic hydrogen, but in conjunction with the hydrogen atom associated with the carbon atom to which the  $\text{NH}_2$  group is attached; opportunity being thus given to the nitrogen atom to become united momentarily by two affinities to

the carbon atom, the formation of the two benzoyl derivatives of opposite activity becomes possible.

I have elsewhere (B.A. Report, 1899, p. 685) contended, in the case of the sulphamic acid formed on sulphonating acetanilide, that when the isomeric change occurs, the ortho-acid is formed from the sulphamic acid if the sulpho-group be, as it were, *let down gently*; otherwise, the para-acid is produced.\*

This, perhaps, is true generally: in other words, it is only when the chlorine is "let down gently" from the chloramine that it enters into the ortho-position.

If we seek to form a picture of the manner in which the equilibrium becomes disturbed, it may be supposed that when the change takes place and an atom of hydrogen becomes separated from the ortho-position in the nucleus, the "centric mechanism" momentarily breaks down and that in consequence the molecule either lapses or is on the point of lapsing into the ethenoid condition. At such a moment, hydrogen chloride might act in one of two ways, and either a chlorine atom might be introduced into the ortho-position, or a hydrogen atom might be restored to this position; in the latter case, two atoms of chlorine would be momentarily associated with the nitrogen, and would either escape as chlorine, or one might combine with a para-atom of hydrogen whilst another atom of chlorine took the place of the hydrogen atom thus removed. The three modes in which the chloramines undergo change are thus provided for. It is obvious that the character of the change might depend on the mass of hydrogen chloride present, and that it might also be affected by the solvent.

Any alteration in the nucleus which diminishes the 'basic' properties of the nitrogen atom would necessarily exercise an influence in retarding the isomeric change, and alterations in the composition of the nucleus would also affect its stability and sensitiveness to change. It is therefore easy to understand that the behaviour of the various chloramines should be different.

Important information as to the manner in which the isomeric

\* It may be here pointed out that the acetyl group exercises an important influence on the occurrence of this isomeric change. It is doubtful whether phenylsulphamic acid can be converted into the *o*-sulphonic acid; to convert it into *p*-sulphonic acid, it is necessary to heat it at about 180°. If, however, it be acetylated by merely heating it with acetic anhydride at 100°, and the product be poured into water and the solution boiled, sulphanilic acid is at once obtained. In the case of Bamberger's experiments, in which a solution of phenylsulphamic acid in acetic acid mixed with a few drops of sulphuric acid was kept for some time at 0°, it is probable that acetylation preceded the formation of *o*-sulphonic acid. It will be desirable to study the influence of different radicals on the occurrence of this isomeric change; although I have obtained the *o*-sulphonic acid from acetanilide, I have not succeeded in preparing it from benzanilide.

change occurs will probably be obtained by determining the velocity with which change is effected under various conditions. It is proposed to undertake such experiments with chloramines when cool and dull weather sets in.

The chloramines are an inviting subject of study for other reasons—and especially on account of their stability under some conditions and their instability under others. We are too much in the habit of regarding compounds as intrinsically unstable which probably are of a comparatively high order of stability in the absence of catalysts capable of determining their alteration; and the disregard of this circumstance has led to the assumption that isodynamic changes especially are the outcome of a state of intramolecular wobble. An increasing body of evidence tends to show that in the cases in contemplation, the process of change is of a complex character and largely extramolecular—in that it involves the co-operation of several distinct molecules and their units in a conducting system.

CHEMICAL DEPARTMENT,  
CENTRAL TECHNICAL COLLEGE,  
EXHIBITION ROAD, S.W.

#### XCIV.—*Derivatives of Cyanocamphor and of Homocamphoric Acid.*

By ARTHUR LAPWORTH.

It is now generally agreed that camphor must contain the complex  $\text{CMe}_2 \cdot \text{CMe} \cdot \text{CO} \cdot$ , but a divergence of opinion still exists with regard to the position of the last carbon atom making up the second ring.

The recent work of Noyes and of Blanc on isolaunolic acid appears to have resulted in the establishment of the formula

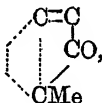
$$\begin{array}{c} \text{CMe}_2 \text{---} \text{CMe} \\ | \qquad \qquad | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CO}_2\text{H} \end{array}$$

for this substance, and would lead, in the absence of other data, to the belief that camphoric acid is a derivative of succinic acid, and that camphor itself contains a tetramethylene ring. Whilst it must be admitted that such an assumption serves to explain the whole behaviour of isolaunolic acid, it is easy to cite facts which are not in accordance with this view. In fact, no matter what formula for camphor may be chosen, it becomes necessary to assume that obscure changes of structure occur on certain occasions. Whilst, therefore,

the Perkin-Bouveault formula offers a ready explanation of just those facts which do not appear to be in accordance with the Bredt formula, and *vice versa*, it may be asserted that the true formula for camphor is still unknown.

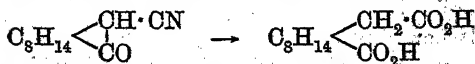
The possibility of attacking the problem in an entirely new manner appeared during the study of camphononic acid (Lapworth and Chapman, Trans., 1899, '75, 989). This acid is a  $\gamma$ -ketonic acid containing the above complex, and, as was pointed out at the time, probably contains the group  $>\text{CO}$  in the place of the  $>\text{CH}\cdot\text{CO}_2\text{H}$  group of camphoric acid, so that, if this point could be definitely established, the inadequacy of any "succinic" formula for camphoric acid would be clearly demonstrated.

One possible method of obtaining a solution of the problem was to prepare from camphor a compound containing the  $\alpha$ -carbon atom united to the second nucleus by an ethylenic linking in this manner,



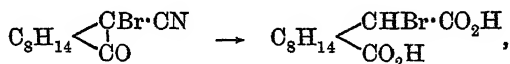
as oxidation of this substance would probably afford the evidence required. It is well known, however, that the  $\alpha$ -halogenated derivatives of camphor do not yield a compound of this type on treatment with bases. It was thought probable that this was on account of the strain which would result in a molecule so constituted, and experiments were therefore made with the object of preparing from camphor a derivative, corresponding with  $\alpha$ -bromocamphor, but in which the brominated atom no longer formed part of a closed chain. The present paper contains an account of observations made during the attempt to obtain this preliminary compound.

It was thought that a derivative of homocamphoric acid,  $\text{C}_8\text{H}_{14}\begin{matrix} \text{CH}_2\cdot\text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{matrix}$ , would probably be the most easily obtained as well as the most readily dealt with. Homocamphoric acid is obtained by hydrolysing  $\alpha$ -cyanocamphor, which, being a  $\beta$ -ketonitrile, breaks down under the influence of alkali, in the same manner as the analogous  $\beta$ -ketonic acids, between the  $\alpha$ - and  $\beta$ -carbon atoms, suffering simultaneous hydrolysis in accordance with the following scheme:



(Haller, *Dissertation*, Nancy, 1879, 29). Much difficulty was at first experienced in obtaining cyanocamphor in sufficiently large quantity, but this was finally overcome by a modification of Bishop, Claisen, and Schaefer's method (*Annalen*, 1894, 281, [351]), namely, by the

ction of excess of hydroxylamine on hydroxymethylenecamphor. Having obtained cyanocamphor, the action of alkalis on its chloro- and bromo-derivatives was examined, as it was expected that these would undergo hydrolysis in the same manner as cyanocamphor, affording chloro- or bromo-homocamphoric acid, thus,



or at least the corresponding hydroxy-acid. It was found, however, that the first action was apparently the replacement of bromine by hydrogen, so that cyanocamphor is regenerated; this affords another example of the tendency of  $\alpha\alpha'$ -di-derivatives of camphor to undergo reduction under the influence of alkali. A further product was a crystalline acid substance having the formula  $\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}$ , probably the half-amide of homocamphoric acid, produced by hydrolysis, either preceding or following the reduction of the bromo-derivative. Experiments on the action of bromine on the nitrile of homocamphoric acid,

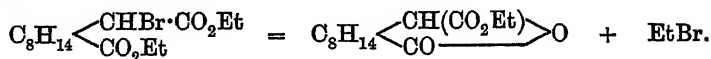
$\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH}_2 \cdot \text{CN} \\ \diagup \quad \diagdown \\ \text{CO}_2\text{H} \end{array}$ , soon showed that no useful object was likely to be served by pursuing the inquiry in that direction. Finally, the behaviour of homocamphoric acid itself towards bromine was examined, but without any important result until the bromination was carried out in the manner detailed in the paper (p. 1063); even then, nothing crystalline could be isolated until nearly anhydrous formic acid was used as a solvent. Under these conditions, however, the monobromo-acid was finally obtained in a pure condition.

$\alpha$ -Bromohomocamphoric acid behaves like homocamphoric acid itself, inasmuch as it exhibits no tendency to lose water and form an anhydride. It is somewhat readily soluble in benzene or chloroform, and in this respect differs from all the related acids, namely, camphoric,  $\omega$ - and  $\pi$ -bromocamphoric,  $\omega\pi$ -dibromocamphoric, and homocamphoric acid itself, which are all nearly, or quite, insoluble in these liquids.

Bromohomocamphoric acid does not yield an unsaturated acid on treatment with excess of alkali, but is converted into a salt of the corresponding hydroxy-acid. The latter does not exist in the free state, but changes to the lactonic acid,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH}(\text{CO}_2\text{H}) \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$ . Camphanic acid is the name used for the corresponding derivative of camphoric acid, so that this substance may appropriately be termed homocamphanic acid.

The behaviour of the diethyl ester of  $\alpha$ -bromohomocamphoric acid towards organic bases was then investigated, and it was found that the action as a rule consisted for the most part in elimination of ethyl

bromide from the molecule, and formation of the ethyl ester of homocamphanic acid, in accordance with the scheme

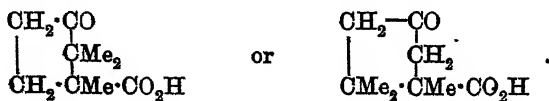


On some occasions, a very small quantity of the ester of a highly insoluble dibasic acid, resembling homocamphoric acid, appeared to be produced, but much difficulty was experienced in increasing the yield of this substance. It was at last found, however, that by heating the bromo-ester with quinoline for a short time at  $210^\circ$ , and subjecting the product to treatment with strong alcoholic potash, a fairly good yield could be obtained.

The new acid, thus produced, appears to be dehydrohomocamphoric acid,  $\text{C}_8\text{H}_{13} \begin{array}{c} \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{array}$ . It readily absorbs bromine, becoming quite altered in properties, although no crystalline brominated products have as yet been isolated. Its solution in dilute sodium carbonate does not at once decolorise ice-cold potassium permanganate, but this is not the first unsaturated acid which has been found to behave in this manner. The potassium permanganate does attack the acid, however, and in the course of 24 hours or less, little or no dehydrohomocamphoric acid can be detected in the liquid.

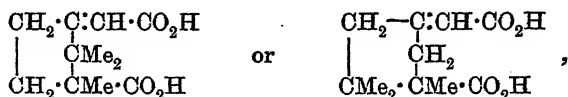
The products obtained by oxidising dehydrohomocamphoric acid in this way were carefully examined, and, as was anticipated, oxalic, camphoronic, and camphononic acids were the principal constituents. Camphononic acid itself was isolated by distilling some of the portion extracted with ether, and in order to make certain that the camphononic acid had not been formed during the heating, a second portion of the product was warmed with a little *p*-bromophenylhydrazine acetate, and a third with excess of a strongly alkaline hydroxylamine solution. In the former instance, nearly pure camphononic acid *p*-bromophenylhydrazone was deposited, and from the latter experiment the unmistakable oxime of camphononic acid was obtained in amount sufficient for complete examination and analysis.

It is thus certain that dehydrohomocamphoric acid, on oxidation with cold dilute potassium permanganate, affords, for the most part, oxalic acid and camphononic acid, together with camphoronic acid, probably arising by further oxidation of the latter. Since camphononic acid is obtained by heating an open-chain tricarboxylic acid (Lapworth and Chapman, *Trans.*, 1899, 75, 989) and yields camphoronic acid on oxidation, it can only be represented by one of the following formulæ :

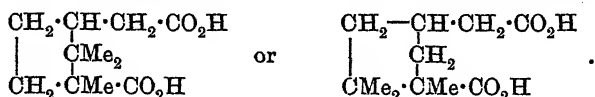




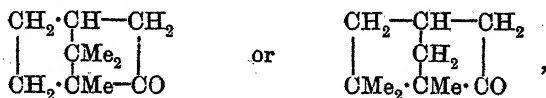
It follows, therefore, that dehydrohomocamphoric acid must have the structure



homocamphoric acid being the corresponding saturated acid, namely:



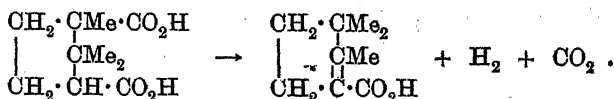
Now, taking into consideration the manner in which homocamphoric acid is obtained from camphor (Haller, *loc. cit.*), as well as the circumstance that camphor is readily obtained by distilling the barium salt of this acid, it would appear to follow, of necessity, that camphor must be represented by one of the two formulæ,



which are those suggested by Brecht and Perkin respectively. It is quite clear that here, as in so many other cases, the Perkin-Bouveault formula offers no simple explanation of the facts.

There is, however, no longer anything which can reasonably be urged in favour of Perkin's formula, more especially as the reasons which led to its suggestion were based on a misapprehension of the true nature of dihydroisolauroic acid. It would appear, therefore, that the evidence, already so strong, in favour of Brecht's formula, is now almost overwhelming, in spite of the difficulty which is met with in explaining by means of it the formation of isolauroic acid and the properties of hydroxydihydroisolauroic acid.

In view of the establishment of the formula of isolauroic acid by Noyes on the one hand (*Ber.*, 1900, 33, 54), and by Blanc on the other (*Compt. rend.*, 1900, 130, 840), the most simple view of the matter which can be taken, in the author's opinion, is that in the formation of campholytic and isolauroic acids from camphoric acid, isomeric change takes place resulting in a new arrangement of the molecule, as follows:



Such a change is not more astonishing than that of isolauroic acid into hexahydroxylic acid when allowed to remain with aluminium

chloride in chloroform solution (Lees and Perkin, *Proc.*, 1900, 16, 20),



or of dihydroisolauroic acid into *p*-xylic acid when warmed with sulphuric acid (Perkin, *Trans.*, 1898, 73, 849).

#### EXPERIMENTAL.

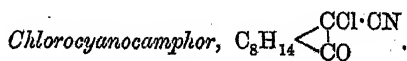
At the commencement of the present work, the various methods which have been used for preparing cyanocamphor were investigated as the substance was required in considerable quantities. The methods originally used by Haller (*Dissertation*, Nancy, 1879, and *Compt. rend.*, 1878, 87, 843) were based on the action of gaseous cyanogen or cyanogen halides on the sodium derivative of camphor, prepared by dissolving sodium in a solution of camphor in boiling toluene, and were found to afford cyanocamphor without much difficulty, but were inconvenient on account of the objectionable nature of the gaseous cyanogen compounds. A later method was that employed by Bishop, Claisen, and Sinclair (*Annalen*, 1894, 281, 351), who found that when the oxime of camphoraldehyde, obtained by the action of hydroxylamine on hydroxymethylenecamphor, is treated with a relatively small quantity of alkali, a certain amount of the sodium derivative of cyanocamphor is formed, and this, on distillation with steam, breaks up into cyanocamphor, which passes over, and sodium hydroxide, which reacts with more of the oxime, the cycle being repeated until about 40 per cent. of the theoretical amount of cyanocamphor is obtained. On examination of this method, it was not found possible to obtain the yield which these workers state is produced, and a number of experiments were therefore made in order to ascertain whether it might not be materially augmented, and the length of time occupied by the operation diminished. It was finally found that, under the following conditions, a nearly quantitative yield of cyanocamphor may be obtained with the greatest ease and in a very short space of time.

Hydroxymethylenecamphor (1 mol.) is covered with a solution of sodium hydroxide (2½ mols.) in about twice its weight in water, and the whole warmed on the water-bath until a homogeneous liquid is obtained. To the cold solution is then added, in one operation, a solution of hydroxylamine hydrochloride (1½ mols.) in the smallest possible quantity of cold water. A certain amount of a yellowish oil is at first precipitated, but this dissolves on shaking. The whole is then heated on the water-bath, under a reflux condenser, which must be kept of being removed with the flask at any moment. As the

temperature rises, a sudden and violent reaction occurs, and the whole liquid boils vigorously; the flask is instantly removed from the water-bath, and cooled as rapidly as possible in a stream of water. It is then seen that conglomerates of a solid material have separated; the flask is once more heated on the water-bath for about 5 minutes to complete the reaction, and, on cooling, the product, which consists of nearly pure cyanocamphor, is separated by filtration, dried, and purified by crystallisation from benzene. It was found to be inadvisable to distil in steam before separating the alkaline mother liquor, as the yield was materially diminished, and a considerable quantity of an oily material of an unknown nature remained in the distilling flask.

One or two observations regarding the crystallographic character of cyanocamphor appear worthy of record. When the substance is distilled with steam, it separates from the distillate in minute plates which are clearly hemimorphic in character, a property which does not hitherto appear to have been attributed to cyanocamphor. The plates are almost invariably pointed at one end, and at the other are terminated by an edge which is at right angles to the length of the crystal; this is not due to fracture, as under a high power the small faces making the edge are clearly distinguishable.

Cyanocamphor is also dimorphous. When melted between slips of glass, it solidifies to a transparent mass intersected by cracks which are arranged at right angles to one another; this modification is cubic. As the temperature falls, a doubly-refracting modification, identical in crystallographic character with the ordinary form of the substance, suddenly makes its appearance at the edge of the material, and quickly spreads until the whole mass has been involved in the change.



This substance is prepared by dissolving cyanocamphor in a little strong sodium hydroxide solution, diluting to a large bulk, and slowly adding to the ice-cold liquid a solution of sodium hypochlorite. A copious, white precipitate results, and the addition of hypochlorite is continued until no further separation occurs. The insoluble material is collected on a filter, washed with water, dried, and crystallised from a mixture of benzene and petroleum. On analysis:

0.2421 gave 0.1665 AgCl. Cl = 17.0.

$C_{11}H_{14}ONCl$  requires Cl = 16.7 per cent.

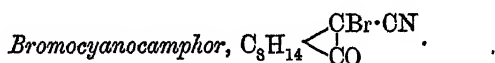
Chlorocyanocamphor is insoluble in water and nearly so in light petroleum, but dissolves fairly readily in most of the other common

media. It crystallises from benzene in small, flat needles or prisms, according to the speed of separation, and on spontaneous evaporation of its solution in dilute alcohol is deposited in beautiful prisms closely resembling those of  $\alpha$ -dibromocamphor. It melts at 98—100°.

The compound is insoluble in hot dilute alkalis or in cold strong alkali; it is attacked by boiling strong alkali, however, and the product obtained is described later in the paper. It is slowly altered when left in contact with alcohol for some weeks, the odour of hydrogen cyanide becoming perceptible.

Crushed fragments of the substance, when examined in convergent polarised light, frequently show biaxial interference figures of wide axial angle; some of these show negative, and others positive, double refraction, being otherwise indistinguishable, so that the axial angle would appear to be nearly 90°.

When melted between slips of glass, the substance sets on cooling to a solid isotropic modification closely resembling that of cyanocamphor; as the temperature falls, a second modification, probably of rhombic symmetry, appears, replacing the cubic form. When the material is now examined in convergent polarised light, a biaxial figure of wide angle is seen here and there, and the bisectrix of the figure, which emerges normal to the field, is probably the obtuse; the double refraction exhibited is always positive.



This substance was first obtained by Haller (*Dissertation*, Nancy, 1879), who prepared it by adding bromine to a solution of cyanocamphor in carbon disulphide. It is more easily made, however, by a method similar to that above described for the preparation of the corresponding chloro-derivative, namely, by adding a solution of sodium hypobromite to a dilute solution of cyanocamphor in sodium hydroxide. It was crystallised from benzene, dried in a vacuum, and analysed.

0.1254 gave 0.0929 AgBr. Br = 31.5.

$\text{C}_{11}\text{H}_{14}\text{ONBr}$  requires Br = 31.2 per cent.

Bromocyanocamphor closely resembles the corresponding chloro-derivative in crystalline character and general properties; thus, it is indistinguishable from it in appearance, general solubility, and mode of crystallisation. Like both cyanocamphor and its chloro-derivative, it exhibits dimorphism. It melts, as stated by Haller, at 74—75°.

*Hydrolysis of Chloro- and Bromo-cyanocamphor.*

Experiments were made with the object of replacing the halogen in the substituted cyanocamphors by means of the hydroxyl group, and for this purpose the substances were heated in alcoholic solution with moist silver acetate and oxide, and with lead hydroxide, but in no case was it found that any large proportion of halogen was removed. On boiling the compounds with dilute alcoholic potash for some hours, a considerable quantity of potassium bromide was formed, and on evaporating the filtrate until free from alcohol, rendering nearly neutral with acetic acid, and distilling with steam, a certain amount of cyanocamphor was obtained. On acidifying the residue in the distilling flask, a precipitate of homocamphoric acid was obtained, and a distinct odour of hydrocyanic acid became noticeable; the presence of the last-mentioned substance was easily shown by the usual tests.

When the halogen derivatives are heated with a strong aqueous solution of caustic soda (40 per cent.), rapid, and even violent, action occurs, and nearly the whole of the material passes into solution. On diluting the liquid and adding acid, no cyanocamphor was liberated, but a copious deposition of a semi-solid material occurred. The substance was extracted with ether, and the ethereal solution washed with water, dried over calcium chloride, and evaporated to dryness. The residue, which gradually solidified, was purified by repeated dissolution in alcohol and precipitation with water, and was finally crystallised from methyl alcohol.

A specimen purified in this manner was dried at 100° and analysed.

0.2559 gave 0.5789  $\text{CO}_2$  and 0.2070  $\text{H}_2\text{O}$ .  $\text{C} = 61.7$ ;  $\text{H} = 9.0$ .

0.3941 „ 22.8 c.c. moist nitrogen at 18° and 755 mm.  $\text{N} = 6.3$ .

$\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}$  requires  $\text{C} = 62.0$ ;  $\text{H} = 8.9$ ;  $\text{N} = 6.6$  per cent.

The substance dissolves sparingly in chloroform, benzene, or light petroleum, but is more soluble in ether, and still more so in ethyl acetate or water. It dissolves fairly readily in alcohol, and separates from the hot alcoholic solution, on addition of water, in the form of very small, well-defined needles, whilst it crystallises from hot alcohol in large prisms. When slowly heated in a capillary tube, it becomes opaque at about 130°, and finally melts and decomposes at about 209—210°.

The properties and composition of this substance indicate that it is identical with  $\alpha$ -homocamphoramidic acid, first obtained by Minguin (*Ann. Chim. Phys.*, 1893, [vi], 30, 512), and therefore has the constitution  $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , so that the action by which it is formed consists in reduction as well as hydrolysis of the halogen derivative, and is similar to that which takes place when  $\alpha$ -dibromocamphor

and other  $\alpha$ -halogen substituted camphors are heated with alkalis, leading to the substitution of hydrogen for an atom of halogen. It would appear probable, therefore, that cyanocamphor is the substance first produced, and that this is subsequently hydrolysed.

*Homocamphoric Acid*,  $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ .

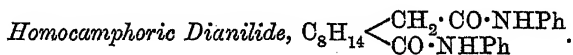
The most convenient method of preparing this acid, which was first obtained by Haller by the hydrolysis of cyanocamphor (*Dissertation*, Nancy, 1879, 29), was found to be the following: cyanocamphor (20 grams) was placed in a flask and covered with a solution of potassium hydroxide (40 grams) in water (120 c.c.), the whole being heated on a water-bath during about 40 hours. The acid obtained by diluting and acidifying the resulting solution weighed, in the crude state, about 16 grams.

The methods of purifying homocamphoric acid which have hitherto been employed appear to be unsatisfactory, as the substance exhibits little tendency to separate in well-defined crystals from any of the usual media, and apparently has always been obtained in a microcrystalline form, except by slow sublimation. As it was very important for the purposes of this investigation to work with pure acid, and to be able to identify it easily and with certainty, the substance was submitted to a close examination from these points of view. It was finally ascertained that, of all the available solvents, nitrobenzene was the most satisfactory. Homocamphoric acid dissolves slowly, but in considerable amount, in boiling nitrobenzene, and separates fairly completely from the solution on cooling, in the form of beautiful, white, glistening needles, which may be separated by filtration, washed with chloroform, and the process repeated until a satisfactory degree of purity has been attained. As a rule, after a second crystallisation, the substance melts at the correct temperature, namely,  $234^\circ$ , which is the melting point given by Bredt (*Annalen*, 1895, 289, 4).

Homocamphoric acid is readily identified, even when somewhat impure, by its crystallographic properties. When melted between slips of glass, it solidifies rapidly to masses of well-formed, flattened crystals which show aggregate polarisation; the axial figures observed, when the mass is examined in convergent polarised light, are usually those characteristic of sections parallel to the axial plane; here and there, however, what appears to be the optic axis of a uniaxial crystal emerges, but seldom, or never, normally to the field; it is possible that the figure observed is in reality that of a biaxial substance with a small optic axial angle, but more probable that the crystals belong to the tetragonal system. The double refraction is positive

and strong. The crystals obtained from nitrobenzene show straight extinction, and are probably crystallographically identical with those obtained by cooling the fused substance.

A considerable number of derivatives of homocamphoric acid were prepared and examined, with the special object of ascertaining which were the most suitable for use in identifying the acid, and a description of the anilide is given, as it is highly characteristic and very easily prepared.



This substance, which was obtained by Haller (*Compt. rend.*, 1895, 120, 1327) by the action of phenylcarbimide on homocamphoric acid, is readily prepared by pouring the crude product obtained by heating homocamphoric acid with phosphorus pentachloride into excess of aniline dissolved in chloroform, the product being worked up by shaking out the excess of aniline with dilute hydrochloric acid, evaporating the chloroform to dryness, and crystallising the residue from acetone. The product thus obtained was dried at 100° and analysed.

0.1701 gave 0.4721  $CO_2$  and 0.1209  $H_2O$ .  $C = 75.7$ ;  $H = 7.7$ .

$C_{23}H_{28}O_2N_2$  requires  $C = 75.8$ ;  $H = 7.7$  per cent.

The substance is somewhat readily soluble in chloroform, and dissolves easily in hot acetone, from which it separates on cooling in beautiful, glistening needles melting sharply at 220—221° (Haller gives 222—223°).

The substance is insoluble in water or alkalis, and, like many of the anilides of dicarboxylic acid, is very stable towards alcoholic potash, although prolonged treatment with very strong potash results in the formation of the half-anilide (Haller, *loc. cit.*) melting at 203°.

When melted on a microscope slide beneath a cover-glass, it slowly solidifies in curious, circular aggregates of small crystals; the crystallisation is greatly retarded by cooling, and at the ordinary temperature is imperceptible; on warming the slide, however, the solidification recommences.

#### BROMINATION OF HOMOCAMPHORIC ACID.\*

Homocamphoric acid is not appreciably affected by bromine, either in the dry or moist state, below about 140°; at this temperature,

\* At the time that the following descriptions of  $\alpha$ -bromohomocamphoric acid and homocamphanic acid were submitted to the Society, the author was not aware that these substances had already been prepared by Rochussen and described in his dissertation (Bonn, 1897). The author has not yet seen this paper, and is indebted to Professor Haller for the information that it is in existence.

however, it is somewhat rapidly attacked, and on opening the tubes in which the action has taken place, much pressure is manifested. If dry materials are used, the contents swell up, forming a white, spongy mass, and usually choke up the capillary tube, so that it was found necessary to immerse the point in water and allow the hydrogen bromide to dissolve. On examining the contents of the tubes, a large proportion was found to be soluble in chloroform, and therefore was not homocamphoric acid; after boiling the material deposited from the chloroform solution with water, however, it lost this property, and was for the most part reconverted into homocamphoric acid.

Experiments were then made, using Volhard's method of bromination, amorphous phosphorus being employed, but again without effecting anything like complete bromination. When phosphorus pentabromide was used, it was found that very little homocamphoric acid was left unaltered, but it invariably happened that, if excess of bromine were used, more than one atomic proportion of bromine entered the molecule, as was ascertained by pouring the product into absolute alcohol and, after fractionation, analysing the esters produced.

Attempts were next made to eliminate hydrogen bromide from the mixture of bromo-esters with alcoholic potash; it was usually found that the greater portion of the product was insoluble in water, indicating that profound changes had been effected during the treatment. On one occasion, the product of bromination was poured into absolute alcohol, the ethyl ester separated, dried, and heated at 180—185° with diethylaniline; hydrogen bromide was eliminated in considerable quantities, and the greater portion of the product decomposed on distillation, but a fraction boiling at 140—150° under 20 mm. pressure was obtained; the distillate was then boiled with alcoholic potash for 6 hours, and the resulting potassium salts examined. On separating from neutral substances, and acidifying the clear aqueous solution, a bulky, white precipitate was produced. This was separated by filtration, dried, and crystallised from dilute acetic acid. On analysis:

0.2334 gave 0.6128  $\text{CO}_2$  and 0.2030  $\text{H}_2\text{O}$ .  $\text{C} = 71.5$ ;  $\text{H} = 9.6$ .

$\text{C}_{10}\text{H}_{16}\text{O}_2$  requires  $\text{C} = 71.4$ ;  $\text{H} = 9.5$  per cent.

The substance obtained in this way is very sparingly soluble in water, but dissolves fairly readily in most of the usual organic media with the exception of light petroleum. It volatilises readily in steam, to which it imparts a somewhat disagreeable, camphor-like odour, and separates from the distillate in beautiful, colourless needles. These, as well as the crystals obtained from dilute acetic acid, melt at 146°, volatilising slightly at this temperature.

The compound is not an acid, as it does not dissolve either in solutions of alkali carbonates or in cold caustic alkalis.



When warmed with strong aqueous potash, however, it slowly dissolves and is not precipitated on diluting the solution with water, but on adding an acid to the dilute solution, a precipitate of unaltered substance is at once produced. These properties are those of a lactone, and from its composition the substance would appear to be produced by elimination of hydrogen bromide and carbon dioxide from a monobromohomocamphoric acid. It is not identical, however, with either Haller's or Forster's campholide.

The solution obtained by dissolving the lactone in alkali and neutralising with carbon dioxide at once destroys the colour of dilute, ice-cold potassium permanganate; unfortunately, owing to the very small quantity of the lactone available, the oxidation products could not be isolated.

*$\alpha$ -Monobromohomocamphoric acid*,  $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$ .

After many failures to prepare the monobrominated acid by the foregoing methods, it was obtained by brominating a mixture of the dichloride of homocamphoric acid and phosphorus oxychloride in the following manner. Homocamphoric acid (10 grams), purified by crystallisation from nitrobenzene and dried at a temperature of  $150^\circ$ , was placed in a round-bottomed flask with a long neck, and gradually mixed with phosphorus pentachloride (20 grams), the whole being afterwards heated on the water-bath for about an hour. After cooling the flask, dry bromine (3.5 c.c.) was added and the whole heated very slowly for about 6 hours, the temperature being raised gradually to  $100^\circ$ ; a further quantity of bromine (1 c.c.) was then added and the heating continued for 1 hour more. The oily product, mixed with powdered ice, was left for 2 days, when it presented the appearance of a semi-solid, gum-like mass which could not be obtained in a crystalline form by the use of the ordinary solvents; when ground up with nearly anhydrous formic acid, however, a slow separation of crystalline matter took place. This was collected, drained on porous earthenware, dried in a vacuum desiccator, and crystallised by dissolving it in a little benzene and adding light petroleum until a slight turbidity ensued. After two or three such crystallisations, the substance was practically pure. A specimen prepared in this manner was dried at  $100^\circ$  and analysed.

0.1702 gave 0.2832  $\text{CO}_2$  and 0.0874  $\text{H}_2\text{O}$ .  $\text{C} = 45.4$ ;  $\text{H} = 5.7$ .

0.2637 „ 0.1678  $\text{AgBr}$ .  $\text{Br} = 27.1$ .

$\text{C}_{11}\text{H}_{17}\text{O}_4\text{Br}$  requires  $\text{C} = 45.1$ ;  $\text{H} = 5.9$ ;  $\text{Br} = 27.3$  per cent.

Bromohomocamphoric acid is very sparingly soluble in water or light petroleum, but dissolves readily in ethyl acetate, acetone, or alcohol, and also in chloroform or benzene. It crystallises from a

mixture of chloroform and light petroleum in rosettes of well-formed needles, and on slow evaporation of its solution in ethyl acetate it separates in small, flat, six-sided leaflets. When slowly heated, it becomes brown at  $170^{\circ}$ , melts slowly, and effervesces at about  $185\text{--}190^{\circ}$ , but is apparently not completely melted at  $220^{\circ}$ . When a capillary tube containing the acid is plunged into sulphuric acid at  $180^{\circ}$ , the substance melts fairly sharply at  $181\text{--}182^{\circ}$ , but slight impurities greatly affect its mode and temperature of fusion.

When the acid is warmed with a dilute solution of sodium carbonate, the resulting solution, after acidification with nitric acid, gives an immediate precipitate with silver nitrate, although this does not occur if the warming has been omitted; moreover, if a solution of the sodium salt is warmed for a few seconds, no precipitate is produced on addition of an acid.

The basicity of the acid was determined by titration against cold standard sodium hydroxide in presence of phenolphthalein; the equivalent found was 152, the calculated number being 146.

When the substance is heated rapidly, it chars and loses much hydrogen bromide; the small quantity of sublimate obtained shows signs of crystalline matter, but its solution in dilute sodium carbonate did not decolorise more than a few drops of dilute potassium permanganate solution, so that an unsaturated acid is probably not present.

A dilute solution of the sodium salt gives no precipitates with salts of barium, calcium, manganese, cobalt, nickel, or cadmium, but affords a white precipitate with lead acetate and a buff one with ferric chloride; with mercuric chloride, no effect is produced in the cold, but opalescence is produced on boiling.

Like homocamphoric acid, this substance shows no tendency to form an anhydride. It was boiled for several hours with acetic anhydride and the solution on evaporation yielded nothing which did not dissolve readily in dilute sodium carbonate.

#### ACTION OF BASES ON $\alpha$ -BROMOHOMOCAMPHORIC ACID AND ITS DIETHYL ESTER.

##### (1) *Formation of Homocamphanic Acid*, $\text{C}_8\text{H}_{14}\left\langle\begin{array}{c} \text{CH}(\text{CO}_2\text{H}) \\ \text{CO} \end{array}\right\rangle\text{O}$ .

In attempting to prepare dehydrohomocamphoric acid by the action of quinoline on the diethyl ester of the bromo-acid, it was found that extensive decomposition and charring occurred, so that the use of diethylaniline was resorted to. When heated with this base at  $170^{\circ}$ , the bromo-ester loses a certain quantity of hydrogen bromide; the reaction, for the most part, however, appears to consist in the elimination of ethyl bromide.

In one instance, the action was allowed to go on for 6 hours, when the diethylaniline was separated from the neutral substances in the usual manner, and the resulting mixture of esters hydrolysed by means of strong alcoholic potash. Although this treatment extended over a period of 5 hours, it was found that the product, on dilution and acidification, was contaminated with large quantities of acid esters which had escaped hydrolysis, and the whole product was therefore boiled with more potash during an additional 12 hours to ensure its complete conversion into the acids. The alcohol was then expelled, the residue diluted with water and acidified, when a very small quantity of a highly insoluble acid separated. The filtrate was extracted with ether, and the acids thus obtained were examined. As they were resinous, they were converted into barium salts and these fractionally crystallised. Some quantity of a sparingly soluble salt was thus obtained, which afforded nearly pure homocamphanic acid on treatment with acids in the usual manner. No other acids could be isolated from the more readily soluble barium salts.

Homocamphanic acid is readily obtained by evaporating an aqueous solution of the sodium salt of bromohomocamphoric acid to dryness, acidifying the residue with dilute hydrochloric acid, and extracting with ether. It is also obtained by heating bromohomocamphoric acid with the calculated quantity of sodium acetate dissolved in glacial acetic acid. It may be purified by drying rapidly at  $150^{\circ}$  and crystallising from benzene. A specimen thus purified was analysed with the following result:

0.1837 gave 0.4209  $\text{CO}_2$  and 0.1213  $\text{H}_2\text{O}$ .  $\text{C} = 62.5$ ;  $\text{H} = 7.4$ .

$\text{C}_{11}\text{H}_{16}\text{O}_4$  requires  $\text{C} = 62.3$ ;  $\text{H} = 7.5$  per cent.

The equivalent of the acid was determined by titration against *N*/10 caustic soda in presence of phenolphthalein; the number found was 217, that required for a monobasic acid of the formula  $\text{C}_{11}\text{H}_{16}\text{O}_4$  being 212. The substance is evidently, therefore, the lactone of  $\alpha$ -hydroxyhomocamphoric acid.

Homocamphanic acid is fairly readily soluble in water, and separates from hot concentrated solutions as an oil which solidifies when the containing vessel is scratched with a glass rod; by slow cooling, it is obtained in the form of glistening needles. It dissolves somewhat readily in benzene or chloroform, and very readily in ethyl acetate, acetone, or alcohol. From benzene, it crystallises in flat, six-sided plates which melt at  $161$ – $162^{\circ}$ , the melting point being unaltered after solidification. These belong to the monoclinic or the anorthic system; in polarised light between crossed nicols the direction of extinction makes an angle of about  $41^{\circ}$  with the longest side; in convergent polarised light, with a  $\frac{1}{10}$  inch immersion objective, an axial

figure of wide angle may sometimes be made out; the bisectrix is probably the obtuse, and shows negative double refraction. In some crystals, however, an axis of a figure of small angle and positive double refraction emerges at the edge of the field.

When melted between slips of glass, the substance solidifies in patches of a radiate structure; in convergent polarised light an optic axis may occasionally be seen, and here and there the bisectrix of a figure of small angle and positive double refraction emerges nearly normally to the field.

Dilute solutions of the sodium salt give no precipitates with salts of barium, calcium, iron, mercury, lead, or even with basic lead acetate. In concentrated solutions, strong calcium chloride occasions a precipitate at once, and barium chloride after several hours.

The stability of the acid is remarkable. It was boiled with moderately strong nitric acid for several days, and on evaporation the residue was found to consist of unaltered acid unaccompanied by any oily oxidation products. A solution of the acid in dilute sodium carbonate had no appreciable effect on dilute potassium permanganate at the ordinary temperature, although slow action appeared to take place at about  $80^{\circ}$ . It was not affected, too, by heating with acetic acid and lead peroxide.

(2) *Formation of Dehydrohomocamphoric Acid*,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{13}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ .

Experiments, carried out with a view of increasing the yield of the highly insoluble acid produced in some of the foregoing experiments showed that a fair quantity could be obtained by the following method.

Diethyl bromohomocamphorate was mixed well with about twice its weight of quinoline, and the whole heated rapidly to about  $210^{\circ}$ , kept at that temperature for about 5 minutes, and then cooled to  $190^{\circ}$ , being allowed to remain at that point for about 2 hours. The esters so produced were then extracted, washed repeatedly with dilute acid, and then hydrolysed. On diluting the product and acidifying, the new acid was precipitated as a bulky, brownish mass; this was collected, purified by conversion into its sodium salt, the solution of which was boiled with animal charcoal for an hour, filtered and acidified. The resulting nearly white acid was collected, crystallised two or three times from strong formic acid, dried, and analysed.

0.1662 gave 0.3768  $\text{CO}_2$  and 0.1138  $\text{H}_2\text{O}$ .  $\text{C}=61.8$ ;  $\text{H}=7.6$ .

0.1852 „ 0.4192  $\text{CO}_2$  „ 0.1279  $\text{H}_2\text{O}$ .  $\text{C}=61.7$ ;  $\text{H}=7.7$ .

$\text{C}_{11}\text{H}_{16}\text{O}_4$  requires  $\text{C}=62.2$ ;  $\text{H}=7.6$  per cent.

$\text{C}_{11}\text{H}_{18}\text{O}_4$  „  $\text{C}=61.7$ ;  $\text{H}=8.4$  „

The equivalent of the acid was determined : 0.1237 gram required 11.8 c.c. *N*/10 caustic soda for complete neutralisation, hence the equivalent found was 105, that required for a dibasic acid,  $C_{11}H_{16}O_4$ , being 106.

Dehydrohomocamphoric acid is readily soluble in methyl or ethyl alcohol, acetic acid, or formic acid, but insoluble in benzene, chloroform, or light petroleum, and practically insoluble in water. It crystallises fairly well from strong formic acid, forming small, four-sided plates, and separates from dilute acetic acid in branched, fern-like crystals. It melts at 190—191°, slight effervescence, but little or no darkening in colour, taking place.

Heated on a microscope slide beneath a cover-glass, it sublimes slightly before melting and the molten substance solidifies on cooling to a mass of elongated plates showing interference colours of low orders in polarised light ; the whole then cracks in innumerable places as the temperature falls, and the effect of the formation of a new modification is produced, as the whole finally exhibits the appearance of aggregate polarisation.

On adding bromine to chloroform containing dehydrohomocamphoric acid in suspension, the colour of the former rapidly disappears, the acid dissolves, and little or no hydrogen bromide is evolved. This indicates that the acid is unsaturated. On adding potassium permanganate to an ice-cold dilute solution of the sodium salt, the colour is not instantly destroyed, but remains for a period depending on the amount added. In the course of several hours, however, considerable quantities of the oxidising material are used up and manganese dioxide is precipitated.

Attempts to isolate bromo-derivatives of the acid were unsuccessful, as were all efforts to prepare from it a lactonic acid. Doubtless, when larger quantities of the acid have been obtained, it will be possible to isolate these products. When the substance is warmed with strong sulphuric acid it dissolves, and gas is evolved, the solution darkening slowly in colour ; on pouring the resulting solution into water, only a slight precipitate of the original substance is obtained.

A dilute solution of the sodium salt gives no precipitates with salts of barium, calcium, cobalt, bismuth, nickel or manganese, or with mercuric or ferrous salts ; with copper acetate, a blue precipitate is obtained, with ferric chloride a copious, buff precipitate results, and white precipitates are formed with silver and mercurous nitrates.

## OXIDATION OF DEHYDROHOMOCAMPHORIC ACID.

*Formation of Oxalic and Camphoronic Acids.*

Whilst, as has already been mentioned, dehydrohomocamphoric acid is not instantly oxidised by potassium permanganate, it is completely altered, if sufficient oxidising material has been used. The oxidation of the acid has been carried out several times with the same results, and although the amount of material dealt with was small, the conclusions drawn from its examination are quite beyond question.

The following is an account of the last experiment made. Five grams of dehydrohomocamphoric acid, purified by repeated crystallisation from formic acid and dilute acetic acid alternately, and melting at 190—191°, were dissolved in dilute sodium carbonate solution, cooled at 0°, and mixed with an ice-cold solution of 12 grams of potassium permanganate dissolved in a litre of water. The whole was then allowed to remain at the ordinary temperature (15—18°) for about 40 hours. The colour of the permanganate had not entirely disappeared, and the excess was therefore destroyed by means of a little sulphurous acid. The liquid was then heated on the water-bath to render it more easy to filter, the manganese dioxide separated by filtration, and the clear liquid evaporated to about 50 c.c.; mixed with a slight excess of nitric acid, boiled to expel carbon dioxide, again neutralised with ammonia, and mixed with excess of calcium chloride solution. A copious precipitate resulted, consisting almost entirely of calcium oxalate; it was insoluble in acetic acid, and yielded nearly pure oxalic acid after treatment with the requisite quantity of dilute sulphuric acid.

The filtrate from the calcium oxalate, after further concentration, was rendered alkaline with ammonia and boiled, when a certain amount of a flocculent precipitate separated. This was almost certainly the calcium salt of camphoronic acid, the presence of which had been proved in the former experiments, and is no doubt due to further oxidation of camphoronic acid.

The filtrate from the calcium camphoronate was rendered strongly alkaline with hydrochloric acid and extracted repeatedly with ether, which was then dried over calcium chloride and evaporated. A crystalline mass remained, which consisted, for the most part, of camphoronic acid, as was proved by the following experiments.

A portion of the crystalline material was transferred to a narrow glass tube and distilled; the distillate in the upper portion of the tube had all the appearance of pure camphoronic acid, and, after removal

and crystallisation from a mixture of benzene and light petroleum, melted at 226—227°, both alone and after admixture with camphononic acid, prepared from homocamphoronic acid.

A second very small portion of the crystalline material was dissolved in a little dilute acetic acid, mixed with a solution of *p*-bromophenylhydrazine acetate, and the whole heated on the water-bath for an hour. On cooling, a separation of minute crystals occurred; these were collected, dried, and crystallised from glacial acetic acid, when brilliant, colourless prisms melting at 193—194° were obtained, having all the properties of the *p*-bromophenylhydrazone of camphononic acid (Trans., 1899, 75, 1002).

The remainder of the material was heated with sodium hydroxide and excess of a solution of hydroxylamine hydrochloride for 2 hours on the water-bath; the whole was then cooled, slightly acidified, and extracted repeatedly with ether. On evaporating off the solvent, a colourless, oily substance was left, which, on trituration with a little methyl alcohol, at once solidified to a white, crystalline mass. This was pressed on porous earthenware and crystallised from methyl alcohol, from which it separated in the magnificent, transparent, unstable rhombohedra so characteristic of the oxime of camphononic acid (Trans., 1900, 77, 465). It melted sharply at 177—178°. On analysis:

0.2409 gave 0.5123 and 0.1778  $H_2O$ .  $C = 58.0$ ;  $H = 8.2$ .

$C_9H_{15}O_3N$  requires  $C = 58.4$ ;  $H = 8.1$  per cent.

The products obtained by oxidising dehydrohomocamphoric acid with dilute potassium permanganate at the ordinary temperature are therefore mainly oxalic and camphononic acids, together with a little camphoronic acid, probably produced by the further oxidation of the camphononic acid.

Most of the expense incurred during the work was defrayed by a grant from the Research Fund of the Chemical Society, and for this the author desires to express his indebtedness. His thanks are also due to Mr. E. M. Chapman, for his assistance during the preparation of the considerable quantities of cyanocamphor which have been employed.

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XCV.—*Asymmetric Optically Active Sulphur Compounds. d-Methylethylthetine Platinichloride.*

By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

SINCE the discovery of the sulphonium compounds by Oefele in 1864, attempts too numerous to be recapitulated here have been made to ascertain whether the sulphur atom is capable of combining with four separate univalent groups, or whether derivatives of apparently quadrivalent sulphur are merely molecular, as distinct from atomic, compounds; many attempts have also been made to determine the space arrangement of the four groups attached to the supposed quadrivalent atom. These attempts have, up to the present, yielded negative or ambiguous results (D. Strömholm, Om sulfin- och tetinföreningar, Upsala, 1899).

Although our earlier attempts (Proc., 1900, 16, 12) to resolve methylethylthetine into optically active components were unsuccessful, we have since succeeded in obtaining an optically active substance,

*d*-methylethylthetine platinichloride,  $2 \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{Cl} \end{array} > \text{S} \begin{array}{c} \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \text{CH}_3 \end{array}, \text{PtCl}_4$ ,

which owes its rotatory power to the presence of an asymmetric quadrivalent sulphur atom, and have thus proved that in compounds of the type  $\text{SX}_4$ , the sulphur atom is truly quadrivalent and that the four groups attached to it are, as in the case of carbon, situated at the apices of a tetrahedron the interior of which is occupied by the sulphur atom.

*d*-Methylethylthetine *d*-Camphorsulphonate,  $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3 \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{CH}_3 \end{array} > \text{S} \begin{array}{c} \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \text{CH}_3 \end{array}$ .

On treating the methylethylthetine bromide of Carrara (*Gazzetta*, 1893, 23, i, 493) in aqueous solution with a molecular proportion of silver *d*-camphorsulphonate (Trans., 1899, 75, 1128), filtering off the silver bromide, and distilling the filtrate at about 40° under a low pressure in a current of air, a residue is obtained which soon solidifies to a crystalline mass in a vacuum desiccator. It is extremely soluble in water, alcohol, or acetone, but may be recrystallised by solution in a little absolute alcohol and addition of anhydrous ether, separation being assisted by strong cooling. Thus obtained, the salt forms colourless, odourless, microscopic prisms melting at 115–117°, and was at first thought by us (Proc., 1900, 16, 12) to be a pure substance because successive fractions had the same composition and practically the same melting point and rotatory power; the apparently pure salt gave the following results on analysis, &c., after drying at 100°



0.1109 gave 0.2002 CO<sub>2</sub> and 0.0724 H<sub>2</sub>O. C=49.24; H=7.25.

C<sub>15</sub>H<sub>26</sub>O<sub>6</sub>S<sub>2</sub> requires C=49.18; H=7.10 per cent.

0.4296 gram made up to 25.1 c.c. with water, gave  $\alpha_D + 0.49^\circ$  in a 200 mm. tube. Whence  $[\alpha]_D + 14.3^\circ$  and  $[M]_D + 52.4^\circ$

0.3843 gram made up to 25.2 c.c. with water, gave  $\alpha_D + 0.43^\circ$  in a 200 mm. tube. Whence  $[\alpha]_D + 14.1^\circ$  and  $[M]_D + 51.6^\circ$ .

Since we have previously shown (Trans., 1899, '75, 1086) that the *d*-camphorsulphonic ion has  $[M]_D + 51.7^\circ$  in aqueous solution, the conclusion that we were here dealing with a pure salt and that no resolution of the base had occurred seemed justified. In order, however, to obtain further evidence, the investigation of this and the salt next described was continued as stated in our preliminary note in February (*loc. cit.*), and the more so in that our work on tin published in May (Proc., 1900, 16, 116) seemed to bear upon the points at issue. During these intervening months, larger quantities of the salt have been prepared and subjected to prolonged fractional crystallisation, with the result that a resolution has been effected. On fractionally crystallising the salt some 40 or 50 times from a mixture of absolute alcohol and ether, a sparingly soluble fraction was obtained which melted at 118—120°, and gave the following results on analysis, &c., after drying at 100°:

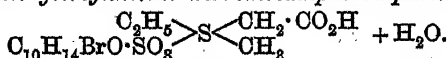
0.1275 gave 0.2304 CO<sub>2</sub> and 0.0839 H<sub>2</sub>O. C=49.27; H=7.31.

C<sub>15</sub>H<sub>26</sub>O<sub>6</sub>S<sub>2</sub> requires C=49.18; H=7.10 per cent.

0.7224 gram made up to 25.1 c.c. with water, gave  $\alpha_D + 1.07^\circ$  in a 200 mm. tube. Whence  $[\alpha]_D + 18.6^\circ$  and  $[M]_D + 68.0^\circ$ .

This material hence seems to be *d*-methylethylthetine *d*-camphor-sulphonate, in which the anion has the molecular rotatory power  $[M]_D + 16.3^\circ$ .

*d*-Methylethylthetine *d*-Bromocamphorsulphonate,



On treating methylethylthetine bromide with silver *d*-bromocamphor-sulphonate (Trans., 1899, '75, 1131) in place of the camphorsulphonate, but adopting otherwise the same procedure, an oily residue ultimately remains which readily solidifies in a vacuum desiccator. This, after several crystallisations from slightly moist acetone, is obtained as a mass of colourless, silky needles melting at 166—168°, and from analysis and rotatory power determinations appears to be a uniform product.

1.7103 lost 0.0571 at 100°. H<sub>2</sub>O=3.34.

0.2455 gave 0.3478 CO<sub>2</sub> and 0.1157 H<sub>2</sub>O. C=38.64; H=5.22.

C<sub>15</sub>H<sub>25</sub>O<sub>6</sub>BrS<sub>2</sub>·H<sub>2</sub>O requires H<sub>2</sub>O=3.88; C=38.87; H=5.83 per cent.

0.3533 gram made up to 25.0 c.c. with water, gave  $\alpha_D + 1.68^\circ$  in a 200 mm. tube. Whence  $[\alpha]_D + 59.5^\circ$  and  $[M]_D + 275^\circ$ .

Since the molecular rotatory power of the *d*-bromocamphorsulphonic ion is about  $[M]_D + 270$  (Walden, *Zeit. physikal. Chem.*, 1894, 15, 196), it seemed that no resolution of the thetine had taken place. Prolonged fractional crystallisation of larger preparations of the salt from moist acetone resulted, however, in the separation of a sparingly soluble fraction having a molecular rotatory power slightly different from the above, although its composition is the same; about 30 crystallisations were undertaken in obtaining this product.

1.8654 lost 0.0666 at 100°.  $H_2O = 3.57$ ;  $1H_2O = 3.88$  per cent.

0.2385, dried at 100°, gave 0.3513  $CO_2$  and 0.1243  $H_2O$ .  $C = 40.17$ ;  $H = 5.79$ .

0.2293, dried at 100°, gave 0.3372  $CO_2$  and 0.1172  $H_2O$ .  $C = 40.10$ ;  $H = 5.67$ .

$C_{15}H_{25}O_6BrS_2$  requires  $C = 40.44$ ;  $H = 5.61$  per cent.

0.6172 gram air-dried salt, made up to 25.1 c.c. with water, gave  $\alpha_D + 3.05^\circ$  in a 200 mm. tube. Whence  $[\alpha]_D + 62.0^\circ$  and  $[M]_D + 287^\circ$ .

0.6594 gram air-dried salt, made up to 25.1 c.c. with water, gave  $\alpha_D + 3.29^\circ$  in a 200 mm. tube. Whence  $[\alpha]_D + 62.7^\circ$  and  $[M]_D + 290.5^\circ$ .

Since ammonium *d*-bromocamphorsulphonate has  $[M]_D + 275^\circ$  in aqueous solutions of about the same molecular concentration as is here used, the examination of the thetine bromocamphorsulphonate, as well as the camphorsulphonate, affords very strong evidence that both contain an optically active thetine of which the ion has about  $[M]_D + 15^\circ$

*d*-Methylethylthetine Platinichloride,  $2 \begin{array}{c} C_2H_5 \\ | \\ Cl \end{array} > S < \begin{array}{c} CH_2 \cdot CO_2H \\ | \\ CH_2 \end{array}, PtCl_4$

On dissolving *d*-methylethylthetine *d*-camphorsulphonate of  $[M]_D + 68^\circ$  or *d*-bromocamphorsulphonate of  $[M]_D + 287^\circ$  to  $+290^\circ$  in absolute alcohol, adding a little concentrated hydrochloric acid and then slowly stirring in an alcoholic solution of the requisite weight of platinic chloride, a yellow, crystalline platinichloride is deposited, which, after exhaustive washing with absolute alcohol, melts with profound decomposition at 177–180°. The salt is very soluble in water, but insoluble in absolute alcohol, and may be crystallised from dilute alcohol; its racemic isomeride is described by Carrara (*loc. cit.*) as melting at 167°.

0.2469 gave 0.1619  $CO_2$  and 0.0802  $H_2O$ .  $C = 17.89$ ;  $H = 3.61$ .

0.1104 „ 0.1391  $AgCl$ .  $Cl = 31.19$ .

0.3558 „ 0.1015  $Pt$ .  $Pt = 28.53$ .

$C_{20}H_{22}S_2O_4PtCl_6$  requires  $C = 17.73$ ;  $H = 3.25$ ;  $Cl = 31.42$ ;  $Pt = 28.71$  per cent.

0.2005 gram of salt from camphorsulphonate, made up to 15 c.c. with water, gave  $\alpha_D + 0.14^\circ$  in a 200 mm. tube. Whence  $[\alpha]_D + 4.6^\circ$  and  $[M]_D + 30.8^\circ$ .

0.3710 gram of salt from bromocamphorsulphonate, made up to 15 c.c. with water, gave  $\alpha_D + 0.22^\circ$  in a 200 mm. tube. Whence  $[\alpha]_D + 4.5^\circ$  and  $[M]_D + 30.2^\circ$ .

The molecular rotatory power  $[M]_D + 30.5^\circ$  of the platinichloride is, as would be expected, just about twice that of the thetine ion,  $[M]_D + 15^\circ$ , deduced from its salts with optically active acids; in spite, however, of this close numerical agreement, we can as yet offer no guarantee that these optically active materials are free from their stereochemical isomerides.

We have thus proved that the asymmetric quadrivalent sulphur atom acts as a centre of optical activity just as does the carbon atom. Since we have previously demonstrated that the same is true of the asymmetric nitrogen (*Trans.*, 1899, 75, 1127) and tin (*Proc.*, 1900, 16, 42 and 116) atoms, we are now justified in concluding that the quadrivalent elements, C, Si, Ti, Zr, Ce, Th, Ge, Sn, Pb, O, S, Se, Te, Cr, Mo, W, and U of groups IV and VI, and the quinquivalent elements N, P, V, Nb, As, Sb, and Bi of group V of the periodic table are in their compounds with four or five groups of atoms, surrounded by groups arranged in tridimensional space, and can thus act as centres of optical activity.

During the present work we have had occasion to examine the conflicting records concerning isomerism possibly occurring in methyl-diethylsulphonium compounds. Krüger (*J. pr. Chem.*, 1876, [ii], 14, 205) and Nasini and Scala (*Gazzetta*, 1888, 18, 67) obtained two sulphonium iodides according as they treated diethyl sulphide with methyl iodide, or methyl ethyl sulphide with ethyl iodide. Klinger and Maassen (*Annalen*, 1888, 243, 193) consider that trimethyl- and triethyl-sulphonium iodides are produced during the latter reaction, and that the platinichlorides of these form a double salt which is naturally not identical with methyldiethylsulphonium platinichloride. We hope shortly to publish details confirming Klinger and Maassen's conclusions, having isolated the same platinichloride from the product obtained by heating methyl ethyl sulphide with ethyl iodide and water, as by crystallising together trimethyl- and triethyl-sulphonium platinichlorides. Any objection to the tetrahedral nature of asymmetric sulphur compounds which might be based on the work of Krüger or of Nasini and Scala can therefore be set aside.

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XCVI.—*A New Method of Estimating Potassium.*

By RICHARD HALIBURTON ADIE and THOMAS BARLOW WOOD.

ERDMANN (*J. pr. Chem.*, 1866, 97, 385) and Sadtler (*Amer. J. Sci.*, 1870, [ii], 49, 189), among other observers, have described double potassium and sodium cobaltinitrites, prepared by precipitating solutions of cobalt salts with strong solutions of potassium or sodium nitrite, and noted the very sparing solubility of potassium cobaltinitrite. This fact has led to the use of a solution of sodium cobaltinitrite (de Koningh's reagent) as a qualitative test for potassium, and the authors' experience of the delicacy of this test has induced them to investigate again the nature and composition of the precipitate obtained, with a view to the possibility of using the reaction for the quantitative estimation of potassium.

Two possible methods of procedure suggested themselves: (1) to precipitate the potassium by a solution of sodium cobaltinitrite, and to weigh the precipitate; (2) to precipitate as before, but to estimate the amount by titrating the nitrite groups with potassium permanganate solution.

For both of these methods, it is necessary to know that the precipitate has a constant composition. To determine this, the authors prepared and analysed several samples, and found them to be dipotassium sodium cobaltinitrite,  $K_2NaCo(NO_2)_6 \cdot H_2O$ .

*Preparation of the Reagent.*—The sodium cobaltinitrite solution was prepared by dissolving 113 grams of cobalt acetate in 300 c.c. of water and 100 c.c. of acetic acid; 220 grams of sodium nitrite were also dissolved in 400 c.c. of water. The solutions were filtered and mixed, and the nitric oxide removed by evacuation. After standing 24 hours, the yellow precipitate, which had separated, was filtered off, and the solution made up to a litre.

*Analysis of the Precipitate.*—The sodium cobaltinitrite solution, when added to an equal volume of a 1 per cent. solution of potassium chloride acidified with acetic acid, gives an immediate yellow crystalline precipitate, which settles in a few minutes. Several samples were made and analysed with the following results:

	I.		II.	III.	Calculated for	
					Mean. $K_2NaCo(NO_2)_6 \cdot H_2O$ .	
K.....	17.2	17.1	—	—	17.2	17.2
Na.....	4.9	5.0	—	—	4.9	5.1
Co.....	13.2	—	13.2	13.0	13.1	13.0
NO <sub>2</sub> .....	61.2	—	—	61.2	61.2	60.8
H <sub>2</sub> O.....	4.1	—	—	—	4.1	3.9
					100.5	100.0

The most convenient mode of analysis was found to be as follows. About 1 gram of the salt was ignited over a burner, by which treatment the cobalt was converted into tricobalt tetroxide,  $\text{Co}_3\text{O}_4$ , whilst the potassium and sodium remained as nitrites. The residue was boiled in water and filtered, the cobalt being weighed as  $\text{Co}_3\text{O}_4$  or as metal, after reduction by hydrogen in a Rose's crucible. The filtrate, after acidification with hydrochloric acid, was evaporated to dryness, gently ignited, and the residue weighed as a mixture of potassium and sodium chlorides.

	I.	II.	Mean.	Calc.
Mixed KCl and NaCl.....	45.3	45.8	45.5	45.5 per cent.

The potassium was estimated in the mixed chlorides by the usual platinic chloride method.

The alcoholic filtrate from the potassium platinichloride was evaporated, the platinum removed by reduction, and the sodium weighed as chloride, and again as sulphate.

The nitroxyl ( $\text{NO}_2$ ) was estimated by boiling the salt with sodium hydroxide solution, filtering off the cobalt hydroxide, which was weighed as tricobalt tetroxide,  $\text{Co}_3\text{O}_4$ , and titrating the filtrate with potassium permanganate solution, after acidification with sulphuric acid, as described later.

The water of crystallisation was not readily given off, even at  $130^\circ$ . It was estimated directly by igniting the salt in a boat in a combustion tube, passing the evolved gases over heated reduced copper gauze to destroy the oxides of nitrogen, and collecting the water in a weighed calcium chloride tube.

So far as the authors have been able to ascertain, the dipotassium sodium salt,  $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ , has not been previously described.

*Solubility of the Salt.*—The solubility of the salt was determined as follows. About 1 gram of the salt was suspended in 200 c.c. of 10 per cent. acetic acid and shaken repeatedly during 3 days; it was then allowed to settle for 24 hours. The slightly turbid liquid was removed by a pipette and filtered, but could not be made perfectly clear, even by filtration through a hardened filter. Fifty c.c. of the filtered solution were boiled with sodium hydroxide solution, filtered from the precipitated cobalt hydroxide, acidified with dilute sulphuric acid, and titrated with  $N/10$  permanganate as before; 0.6 c.c. was required, which makes the solubility rather less than 1 part of the salt in 20,000.

*Gravimetric Estimation.*—The definite composition and the insolubility of this salt make it suitable for the gravimetric estimation of potassium, as the following results show: 10 c.c. of a 1 per cent. solution of pure potassium chloride were precipitated by 10 c.c. of the sodium cobaltinitrite reagent, with the addition of 1 c.c. of strong acetic acid.

The precipitate was allowed to stand overnight, filtered either through a weighed Gooch filter, or weighed filter paper, washed with 10 per cent. acetic acid until the washings were colourless, and, finally, once with water, dried at 125° until the weight was constant, and weighed.

	I.	II.	III.	Mean.	Taken.
Wt. of KCl, calc. from wt. of $K_2NaCo(NO_2)_6 \cdot H_2O$ ...	0.103	0.101	0.096	0.1	0.1 gram.

These numbers suffice to show that, under the conditions of the experiment, the potassium is completely precipitated, and that the method gives accurate results with very little trouble.

To secure reliable results, it is most important to precipitate from a solution containing between 0.5 and 1 per cent. of potash,  $K_2O$ . At this concentration, the precipitate settles readily, and in such a physical state that it is easily retained by a filter. At greater dilutions, the precipitate settles out very slowly, adheres very firmly to the sides and bottom of the beaker, and passes through the filter so persistently that at a concentration of 0.2 per cent., the weight of precipitate obtained was 6 per cent. below the calculated, whilst at 0.1 per cent. only two-thirds of the calculated amount could be collected. The deficiencies are far larger than the solubility of the salt could account for, and are apparently due to mechanical difficulties in collecting so fine a precipitate.

*Volumetric Estimation.*—The precipitation and washing are carried out as above; the filtration must, however, be made through asbestos in a Gooch filter, as paper interferes with titration by potassium permanganate. When washed, the precipitate and the asbestos plug are blown out of the Gooch filter into a beaker, and boiled with dilute sodium hydroxide solution. The asbestos and the precipitated cobalt hydroxide are filtered off, and the filtrate containing all the nitrite of the precipitate is made up to 100 c.c. The authors find the most convenient method of titrating to be as follows.

20 c.c. of the solution are acidified and rapidly titrated by  $N/10$  potassium permanganate solution. As some loss of oxides of nitrogen may occur on acidification, a second and more accurate titration is made by adding the volume of permanganate solution thus found to the nitrite solution before acidification, and then adding more permanganate solution until a permanent colour is produced. As an example, 20 c.c. took 16.3 c.c. of permanganate solution when acidified first, but when to another 20 c.c., 16.3 c.c. of the permanganate solution were added, followed by dilute sulphuric acid, it was found that a further addition of 6.1 c.c. of permanganate solution was required to produce a permanent coloration. The end point is determined quite sharply by 1 drop of permanganate solution producing a colour which lasts for 1 minute.

*Estimation of Potash in Manures and Soils.*—The method is very suitable for the estimation of potash in such commercial fertilisers as muriate, or sulphate of potash, kainite, &c., or in soils. The method adopted by the authors for fertilisers is as follows: weigh out 10 grams of muriate or sulphate of potash, or 40 grams of kainite, and dissolve in water, making the solution up to 1 litre. Filter off a portion through a dry filter, take 10 c.c., add 10 c.c. of the sodium cobaltinitrite reagent and 1 c.c. of acetic acid, allow to stand until the precipitate has settled, pass through a Gooch filter, and proceed to the volumetric estimation as above.

The following results have been obtained :

<i>Commercial Muriate of Potash :</i>		K <sub>2</sub> O per cent.
By cobaltinitrite volumetric method .....		49.67
By platinic chloride gravimetric method .....		49.64

<i>Commercial Sulphate of Potash :</i>		I.	II.
By cobaltinitrite volumetric method.....		50.05	50.82
By platinic chloride gravimetric method ...		50.80	

<i>Kainite :</i>	I.	II.	III.
By cobaltinitrite volumetric method .....	12.22	11.94	12.70
By platinic chloride gravimetric method...	11.98	12.07	12.53

For soils, the authors have found the following method to give very satisfactory results. The soil is extracted by heating 10 grams in a loosely stoppered Jena glass flask with 20—30 c.c. of strong hydrochloric acid for 48 hours. The solution is then freed from all bases which might interfere with the method, by boiling with excess of sodium carbonate. The precipitated bases are filtered off, and the solution concentrated, after addition of acetic acid, to 10 c.c., or to a volume which gives the concentration of potash recommended above. Ten c.c. of the sodium cobaltinitrite reagent are now added, with more acetic acid if necessary, and the precipitate allowed to settle. The volumetric estimation is now carried out as before.

The following results have been obtained by various extractions of the same peaty soil under different conditions. The solution from each extraction was divided into aliquot parts, and comparative estimations of the potash made by the cobaltinitrite volumetric and by the platinic chloride gravimetric methods :

<i>Peaty Soil :</i>		K <sub>2</sub> O per cent.				
		I.	II.	III.	IV.	Mean.
By cobaltinitrite volumetric method	}	1.09	1.20	1.06	1.05	1.10
By platinic chloride gravimetric method		1.11	1.25	0.98	0.97	1.08

The results as a whole show that the cobaltinitrite volumetric method is nearly as accurate as the methods hitherto available for estimating potassium by means of platinum, whilst it is much easier to work and presents no special difficulties.

CAMBRIDGE.

## XCVII.—*Notes on the Chemistry of Chlorophyll.*

By LEON MARCHLEWSKI, Ph.D., and C. A. SCHUNCK.

DESPITE the great amount of work performed and published in regard to the question of the real spectrum of chlorophyll, scientific opinion on this subject is by no means unanimous. Chlorophyll is notoriously one of the most changeable compounds known, and the disregard of this circumstance has led several authors to ascribe to substances, isolated by methods in which the action of chemical reagents has not been excluded, the name of chlorophyll which they cannot possibly claim.

### 1. THE SPECTRUM OF CHLOROPHYLL.

In order to be able to ascertain whether a certain process leads to the isolation of unaltered chlorophyll, or whether the product under observation is in fact a chlorophyll derivative, two methods have been used, one a physical and the other a chemical one.

The physical method is the well-known optical one. The spectroscopical properties of the product isolated are compared under the same conditions with the properties of a solution of chlorophyll which has not been under the influence of any reagents whatever.

As is well known, crude alcoholic green leaf extracts produce an absorption spectrum in the visible region which consists of four bands between the lines B and F, and are also characterised in the more refrangible region, as one of us has shown (*Proc. Roy. Soc.*, 1898, 63, 389), by three bands situated between F and the potassium  $K_{\beta}$  line, the first of which by artificial light is visible to the eye.\*

\* As regards the spectrum given by the living leaf, our observations, using direct sunlight as the source of light, show that in a thin leaf only the characteristic band in the red is visible accompanied by a distinct lighter shading on its more refrangible side, the rest of the visible spectrum being continuous. In a denser leaf, the band and shading become of the same intensity, forming a broad intense band, and at the same time there is an indication of a band in the vicinity of the F-line. A still denser leaf cuts off all the visible rays more refrangible than the  $\delta$ -lines, but shows an indication of a band adjacent to D situated on its less refrangible side, whilst the band in the red has become still broader. This band, as seen in a thin leaf, lies approximately between  $\lambda$  6975 and  $\lambda$  6700, the shading extending to  $\lambda$  6500. In



The relative intensity of the three first bands between B and F is almost the same in all freshly prepared solutions, but the fourth band in the vicinity of the line E varies, being even sometimes darker than the third band, and sometimes hardly visible, a fact which suggests the supposition made by E. Schunck (*Annals of Botany*, 1889, 3, 65), that this fourth band does not belong to chlorophyll, but to some derivative of it. The question now arises whether these four bands in the less refrangible region, or at least three of them, and the three in the more refrangible region characterise a chemical individual, or whether they are caused by several substances.

The majority of observers contend that the bands exhibited by a crude leaf extract between the lines B and F, or at least three of them, are indeed caused by a chemical individual—chlorophyll—a view which we also share, and we believe that the three bands in the more refrangible region are also due to the same individual, for the following reasons.

It is well known that crude alcoholic chlorophyll extracts contain at least one green colouring matter and several yellow substances, the xanthophylls. It is possible, however, using the following method, based on the very elaborate and important observations of Sorby (*Proc. Roy. Soc.*, 1873, 21, 442), to get rid of the greater portion of these accompanying colouring matters and at the same time to cause no alteration in the chlorophyll proper. This method, which is explained fully in the second part of the paper, depends upon the difference of solubility of the coloured constituents of crude chlorophyll extracts in alcohol or carbon disulphide, when the alcoholic extract is agitated with successive quantities of the latter, and by which means the chlorophyll can be obtained comparatively free from the other coloured constituents of the crude extract. On now examining the spectrum, it will be found to be exactly similar to that of the crude extract, with the exception that more of the ultra-violet is visible extending in our photographs as far as O,\* this fact being no doubt due to the absence of certain members of the xanthophyll group which produce a general obscuration in this region of the spectrum. The solutions also appear to be slightly greener in colour, due to the absence

an alcoholic extract of chlorophyll of such a strength as to show the spectrum to the best advantage, the band in the red lies between  $\lambda$  6850 and  $\lambda$  6400, and in the weaker solutions between  $\lambda$  6750 and  $\lambda$  6600, so it appears that there is a shifting of this band still further into the red in the living leaf, and the spectrum given by the leaf appears to us to be characterised almost solely by this band, whereas the spectrum of an alcoholic extract is characterised by at least three distinctive bands between B and F.

\* The examination of the violet and ultra-violet region was accomplished by means of photography, an Iceland spar prism and quartz lenses being used, and the source of light was a Welsbach incandescent gas mantle of 60 candle-power.

of the xanthophylls. These facts make it evident that the colouring matters of the xanthophyll group have no influence upon the bands of a crude leaf extract, either in the less or more refrangible region of the spectrum, and that the spectrum as shown by these crude solutions is indeed most probably due to a chemical individual known as chlorophyll.

This method does not, however, solve the question of the origin of the fourth band situated near the line E, the solubility of the derivative which produces this band in alcohol or carbon disulphide seeming to be about the same as that of chlorophyll itself. To achieve this result a method mentioned first by Kraus ("Zur Kenntniss der Chlorophyllfarbstoffe," 1872) may be used, which consists in treating crude extracts with benzoline. This solvent takes up the green colouring matter along with a considerable quantity of the yellow substances. By washing the first benzoline extract repeatedly with alcohol and by experimenting in absence of direct light, a benzoline solution is at last obtained which shows no traces of a band in the vicinity of the line E, especially in the case of extracts of *Ficus repens*, which were used throughout these experiments and give a very typical chlorophyll spectrum with which to start; the fourth band is but faintly visible. The above result, that chlorophyll when purified gives a spectrum which is characterised in the less refrangible region by three bands, one in the red, starting approximately at B and overlapping C, another in the orange, and a third beyond D, and three bands in the violet and ultra-violet situated between F and K<sub>s</sub>, we consider to be an accurate description of the spectroscopic properties of unaltered chlorophyll, and we believe that a product isolated by any method whatever cannot be termed "chlorophyll" unless it possesses this spectrum.

As regards the chemical criterion for unaltered chlorophyll, it must be admitted that a product deserves the name of "chlorophyll" only if it yields under the influence of acids phyloxanthin and phyllocyanin, or at least the latter, by the prolonged action of the acid.

Having described the conditions under which, in our opinion, a substance may be called "chlorophyll," we will now describe the results of our experiments relating to a substance termed by Hartley (Trans., 1891, 59, 106) "blue chlorophyll," which, according to him, possesses all the optical properties of normal chlorophyll. Hartley's conception of the latter is not, however, in agreement with our own. This author maintains that a "solution of leaf green, made with cold alcohol of 98 per cent. by extracting the colour from minced ivy leaves, either with or without washing, has the properties of the ivy leaf in that it absorbs nearly all the red rays and the green rays near to the red end of the spectrum, the yellow and orange rays are dimmed,

but the green is wholly transmitted." If this solution be diluted with water and shaken up with benzene, the latter will dissolve a substance which, according to Hartley, possesses exactly the same optical properties as his "blue chlorophyll"; a fact which is considered by him to be a proof of the soundness of his method for isolating the "blue chlorophyll." We are sorry to say that, after repeating Hartley's experiments, we arrived at the conclusion that his description of the chlorophyll spectrum as shown by cold leaf extracts or benzene extracts, obtained by adding water to the former and shaking up with benzene, is erroneous and that these spectra do not differ in any way from the one considered by us the normal chlorophyll spectrum (except as regards the fourth band), but differ radically from the spectrum of Hartley's "blue chlorophyll."

Hartley's method for the isolation of "blue chlorophyll" consists in the treatment of cold alcoholic leaf extracts with a saturated aqueous solution of barium hydroxide. There is formed a green precipitate which is washed with water, alcohol, and chloroform in order to remove the so-called "yellow chlorophyll," the nature of which is discussed in the second part of the present paper. The precipitate obtained is treated with a mixture of boric acid, glycerol, and alcohol; the acid decomposes the barium compound and the colouring matter liberated dissolves in the alcohol. The solution thus obtained appeared of a fine bluish-green, not unlike solutions of alkachlorophyll. A portion of it was diluted with water and extracted with ether, and the ethereal solution obtained compared with an ethereal solution of chlorophyll prepared by extracting the original alcoholic leaf extract with ether after water had been added to it. The ethereal solution of Hartley's colouring matter showed a very different spectrum from that of chlorophyll. When observed in concentrated solution, it exhibits four bands, of which the first in the red is very broad and intense, and corresponds approximately in position to that of the first characteristic chlorophyll band; the remaining three bands, especially the one furthest away from the red end, are extremely faint. That part of the spectrum in which appears the second chlorophyll band is quite clear, no band being present. A still greater difference is noticeable in comparing very dilute solutions. If the ethereal solution of Hartley's "blue chlorophyll" is diluted to such an extent that the faint bands disappear altogether, the previously broad band in the red appears to be split into two, whereas a corresponding splitting of the first band of chlorophyll is not noticeable at any dilution. From the foregoing it will be seen that Hartley's chlorophyll exhibits very marked differences in comparison with ordinary chlorophyll solutions and the conclusion must be formed that the barium hydroxide used for its isolation has

undoubtedly some chemical effect on the colouring matter present in the original green leaf extracts.

- The first suggestion which might be put forward in order to explain the difference observed is that Hartley's chlorophyll is in reality alkachlorophyll, that is, a derivative of chlorophyll obtained by the action of caustic alkalis on chlorophyll in boiling alcoholic solutions. Indeed the two substances have certain properties in common, but there also exist certain differences which it would be at present premature to discuss.

We now proceed to describe the results obtained by the action of acids on Hartley's "blue chlorophyll." An ordinary alcoholic solution of chlorophyll, when treated with hydrochloric acid, yields phylloxanthin and phyllocyanin, two substances of well known physical properties. If Hartley's colouring matter is true chlorophyll, it ought also to give these two derivatives of chlorophyll, or at least phyllocyanin, the last product of the action of acids on chlorophyll. As a matter of fact, a very different result has been obtained. The bluish-green alcoholic solution of Hartley's "chlorophyll," which, however, contains some glycerol, changes to greyish-blue on adding to it some concentrated hydrochloric acid. The mixture, on being poured into water and extracted with ether, gives a greyish-brown, ethereal solution which, on being examined spectroscopically, shows the well known spectrum of phyllotaonin consisting of six bands, but not the phyllocyanin spectrum of five bands. This shows that, towards acids, Hartley's colouring matter behaves quite differently from chlorophyll, and in comparison with the behaviour of alkachlorophyll a difference is noticeable in so far as the last named derivative invariably gives an ether of phyllotaonin on treatment with hydrochloric acid in an alcoholic solution.

It is difficult to say at present whether these facts point to an actual difference between Hartley's "blue chlorophyll" and alkachlorophyll, or whether the glycerol present in the solution of Hartley's chlorophyll has anything to do with the matter. We may add, however, that on two occasions the ethereal solution of the decomposition product of Hartley's chlorophyll by acids gradually changed its spectrum of six bands into that of an ether of phyllotaonin with five bands, two being situated in the red and three in the green and blue, a fact which, however, seems to prove that only the phyllotaonin present in the ethereal solution might have changed into ethylphyllotaonin under the influence of ethylchloride, which no doubt could have been present in small quantities in the acid solution.

In another respect, Hartley's blue chlorophyll behaved exactly like chlorophyll. If its boiling alcoholic solution is treated with an acetic acid and afterwards evaporated almost to dryness,

the residue suspended in water, and the mixture extracted with ether, a solution is obtained which shows the spectrum of acetylphyllotaonin, which, as is well known, is identical with that of ethyl phyllotaonin. Alkachlorophyll, treated in the same manner, behaves similarly, giving also acetylphyllotaonin. As regards the absorption in the violet region of the spectrum, Hartley's blue chlorophyll differs considerably from chlorophyll, for instead of the three bands characteristic of the latter, it possesses, like alkachlorophyll, only a single band overlying the potassium  $K_\beta$  line.

In conclusion, we may sum up our experiences with Hartley's "blue chlorophyll" as follows. It is not unaltered chlorophyll; barium hydroxide when acting on chlorophyll causes, even at the ordinary temperature, some chemical change; the substance so produced is closely related to alkachlorophyll, and possibly identical with it. When treated with acids, it yields phyllotaonin or its derivatives, but not phylloxanthin or phyllocyanin. In connection with physiological problems, Hartley's statement in regard to the chlorophyll spectrum must lead to errors, relating, as it does, to a derivative of chlorophyll never present in the living plant, and not to chlorophyll itself.

## 2. EVIDENCE FOR THE EXISTENCE OF SEVERAL CHLOROPHYLLS.

On addition of barium hydroxide to a crude alcoholic chlorophyll solution, the greater portion of the green colouring matter appears to be precipitated at once, leaving the filtrate of a yellowish-green colour; on addition of more barium hydroxide and allowing to stand, a further precipitation takes place, the resulting filtrate finally being of a yellow colour.

Examination by the spectroscope shows this *resultant* yellow filtrate to possess no absorption bands in the red, yellow, or green, but in the more refrangible region of the spectrum to have the four bands situated between the lines F and L, shown by one of us (*Proc. Roy. Soc.*, 1899, 65, 177) to be characteristic of the xanthophyll group of yellow colouring matters which accompany chlorophyll in healthy green leaves, and are extracted along with it by means of alcohol. The first of these bands is plainly visible to the eye, and lies just beyond the line F; the presence of the others is made evident by means of photography. We have thus in the resultant filtrate the accompanying yellow colouring matters of the xanthophyll group.

On examining the *initial* filtrate, which is, as before stated, of a yellowish-green colour, a band in the red makes its appearance, however, as has been observed by Hartley, to whom this method of separation is due (*loc. cit.*). This, on concentration, is as broad and almost as intense as the first characteristic chlorophyll band observ-

able in all crude alcoholic extracts, but not in the same position, the band in the filtrate being shifted about a quarter of its width towards the violet. At the same time, there is no indication of the second, third, and so-called fourth chlorophyll bands, the yellow and green being continuous. On dilution, until the band in both becomes narrow, the more refrangible edge of the band in the crude extract just overlaps the less refrangible edge of the band in the filtrate, the latter being now about half the intensity of the former, the centres of the two bands being approximately  $\lambda$  6655 and  $\lambda$  6450. On further dilution, the spectrum beyond F is that of the xanthophyll group of yellow colouring matters, consisting, as before, of four bands. As the latter group of yellow colouring matters by themselves show no band in the red, we must conclude that another colouring matter besides chlorophyll is present, and it is this mixture of colouring matters contained in the filtrate that we gather Hartley (*loc. cit.*) has designated by the term "yellow chlorophyll." That this additional colouring matter is distinct from chlorophyll is shown by its behaviour towards acids. When crude chlorophyll solutions are acted on with hydrochloric acid, the phylloxanthin spectrum, consisting of four bands, is first observed, and finally that of phyllocyanin, composed of five bands. In the case of this so-called "yellow chlorophyll," however, even after prolonged action of hydrochloric acid, only two faint, narrow bands appear, coinciding in position with the second and third phylloxanthin bands, and a narrow, darker one in the vicinity of the fourth phyllocyanin band, but the resulting spectrum does not seem to bear much resemblance to either that of phylloxanthin or phyllocyanin. A difference is also observable in the more refrangible region, for on adding a drop of hydrochloric acid to a small portion of a very dilute solution of the crude leaf extract, two pronounced bands are formed on each side of the potassium  $K_2$  line, whilst in the case of the filtrate containing the "yellow chlorophyll" only one band is produced, overlapping this same line; further, this band is not due to the action of the acid on the xanthophylls, for on acting on them alone in the same manner, no such band is formed, the action of acid in this case only tending to decrease the intensity of the bands. This is a very delicate reaction, for in order that the bands shall be visible on the photographic plate to the best advantage, the solutions must be *very* dilute. This additional colouring matter, like chlorophyll, can be removed from its solutions by means of animal charcoal, leaving the xanthophylls in solution, the process being one for obtaining the latter free from the green constituent of the crude leaf extracts. It was mentioned that the colour of the filtrate containing this additional colouring matter was a yellowish-green, but we are led to believe that the colour is due to the xanthophylls, and that if it were possible

to get rid of the latter, the filtrate would be green. The reason for this assumption is based on the fact that if the yellowish-green filtrate be agitated with carbon disulphide, having the alcoholic solution of such a strength that a separation takes place between the two, the carbon disulphide will take up a greater part of the xanthophylls in preference to this additional colouring matter, so that after a number of washings with the solvent the alcoholic solution becomes much greener, in fact almost as green as that of the crude extract, and shows the band in the red as before, with the yellow and the green continuous. Much of this colouring matter is, however, lost by being taken up by the carbon disulphide in the process of washing, and there still remains mixed with it in the alcoholic solution some of the xanthophylls, as proved by the spectrum in the violet and ultra-violet being the same as is shown by a yellow colouring matter or matters that can be separated in a similar manner from the other members of the xanthophyll group after the green constituent has been removed by means of animal charcoal. There is thus good evidence that a colouring matter is present in addition to true chlorophyll and the yellow colouring matters of the xanthophyll group, but in what proportion it occurs cannot at present be satisfactorily answered. We think it is present in a relatively small quantity compared with true chlorophyll, and not in sufficient amount to affect the first characteristic band in the crude alcoholic chlorophyll extracts.

Hartley states that, in addition to the barium compound of his "blue chlorophyll," he also obtained a considerable quantity of the barium compound of his so-called "yellow chlorophyll." Unfortunately, we have failed to identify the latter compound, as the precipitate which was formed from the yellowish-green filtrate (leaving the solution yellow, showing no band in the red, and, as we proved, consisting of the xanthophylls), after being treated with boric acid, gave a similar compound to that obtained from the initial precipitate. Whether this fact may be taken as a proof that with baryta true chlorophyll and this so-called "yellow chlorophyll" form the same compound, it is at present difficult to decide.

Our observations of its spectroscopic properties coincide with Hartley's with respect to the band in the red. With regard to the more refrangible part of the spectrum, we differ from him, as he states that his "yellow chlorophyll," even in very thin layers of a dilute solution, gives a powerful absorption band extending from  $\delta$  to  $H_2$ . We find only the bands characteristic of the xanthophyll group in this region, but this does not prove that if the substance were freed from the xanthophylls it would not have a peculiar spectrum of its own in this region. All we can say is that this method furnishes evidence of the existence of a colouring matter in addition to chlorophyll and the

xanthophylls, which has a red fluorescence, imparts a green colour to its alcoholic solutions, and is characterised by a band in the red which is more refrangible than that due to chlorophyll as seen in its crude alcoholic extracts.

The existence of this colouring matter can be shown, however, by another method, namely, that of Sorby before mentioned (*loc. cit.*), which consists in the fractional separation of the alcoholic extracts of chlorophyll by means of carbon disulphide.

Our experiments were made on similar lines to Sorby's, using, as before, a strong alcoholic extract of *Ficus repens*. This was shaken up four or five times with an equal volume of carbon disulphide, whereby the whole of the green constituent and the greater portion of the yellow colouring matters composing the xanthophyll group are taken up by the solvent, leaving in the alcohol some of the xanthophylls, which are more soluble in it than in carbon disulphide. We have thus all the colouring matters capable of being taken up by carbon disulphide divided into several fractions, according to their relative solubility. The first carbon disulphide fraction contains nearly the whole of the chlorophyll, together with a large portion of the xanthophylls, and has an olive-green colour. The subsequent fractions contain small, decreasing quantities of chlorophyll and the remainder of the xanthophylls, the latter, however, greatly preponderating, the colour of the fractions now varying from an amber-brown to a rich amber colour. On a spectroscopic examination, the *second* of these carbon disulphide fractions, in addition to the bands due to chlorophyll, which are now only feebly exhibited, has an additional narrow band in the red in close proximity to, and on the more refrangible side of, the first chlorophyll band, the latter being perhaps a little broader and more intense; the other carbon disulphide fractions only feebly exhibit this additional band. The *first* fraction shows the same spectrum as the alcoholic extract, with this exception, that the bands are shifted about a quarter of their width towards the red end, this being due to the difference in the solvent. On diluting this fraction until the first band in the red becomes narrow, a distinct shading is visible on its more refrangible side, not quite as broad as the band itself, but corresponding in position with the more refrangible of the above double bands, as seen in the second fraction. If we examine this second carbon disulphide fraction in alcohol (having evaporated it to dryness and taken up with alcohol), the more refrangible of the two bands now appears only as a distinct shading in dilute solutions, and not detached from its companion as when carbon disulphide is used as the solvent, but on comparison with the filtrate obtained by the baryta method, this shading corresponds in position with the band in the filtrate. We thus, by this method, have additional evi-



dence for the existence of the so-called "yellow chlorophyll," although it seems impossible in this case to free it from a certain amount of true chlorophyll—the "blue chlorophyll" of Sorby. The reason why the band appears double in a carbon disulphide solution, and only in the form of a shading in alcohol, is due to the different effect of the two solvents, the position of the more refrangible of the two bands being about the same in both, but the less refrangible one is shifted more towards the red end in carbon disulphide than in alcohol. Finally, the reason why it does not appear as a separate band in the first carbon disulphide fraction, but only as a shading, is that the colouring matter producing it appears to be less soluble than true chlorophyll in carbon disulphide, and consequently the latter is now present in a much greater relative quantity than it was in the second fraction, so that even on dilution a separation is impossible. That this explanation meets the case, can be shown by washing the first carbon disulphide fraction with methylated spirit, by which means we can take the colouring matters back into alcoholic solution, but in different relative proportions, for on adding water to the first spirit extract, which will throw down the colouring matters along with the dissolved carbon disulphide, we get a spectrum in which the band in the red is as distinctly double as in the second carbon disulphide fraction of the original separation. As in the baryta method, we can find by this process no other bands except the solitary one in the red to characterise the substance. The various carbon disulphide fractions give in the violet and ultra-violet either the characteristic spectrum of the crude chlorophyll extract, namely, three bands situated between F and K<sup>β</sup>, or those of the xanthophyll group, according as one or the other preponderates. In all these carbon disulphide fractions, however, there is a pronounced band in the green situated on the less refrangible side of the F line, which, when the fractions are observed in alcohol, is not visible, and no doubt is the chief cause of the difference in the colour of the fractions when observed in alcohol and carbon disulphide. This band, we find, corresponds in position to the first of the bands of the xanthophyll group when dissolved in carbon disulphide, this solvent having a very considerable shifting effect upon them as compared with alcohol. As the presence of the xanthophylls can be proved in all the carbon disulphide fractions, and as both chlorophyll proper and the so-called "yellow chlorophyll" can be removed by means of animal charcoal without affecting this band, we may safely conclude that it belongs to the xanthophyll group. Sorby states that in addition to the band in the red, his "yellow chlorophyll" has a band in the green, but we think from the description of his separation that it was due to some of the xanthophylls which he had not removed; for although

carbon disulphide in the first instance takes up a large quantity of the xanthophylls, a goodly quantity is redissolved on washing with methylated spirit. A portion, at any rate, of this group is therefore equally soluble in both solvents, and thus this colouring matter cannot be freed entirely from the xanthophylls.

The reason why the band of the so-called "yellow chlorophyll" does not influence the spectrum of the crude alcoholic leaf extracts remains to be discussed. We believe it is because of the great preponderance of true chlorophyll, whose band in the red, in strong solutions, more than covers the space occupied by the one due to the "yellow chlorophyll," whilst on diluting the solution to such a strength that it should be possible to see it, the quantity has become too small to affect the spectrum. This view is corroborated by uniting the different carbon disulphide fractions, which amounts to having the whole extract dissolved in this solvent. On then examining the spectrum in a moderately strong solution, the presence of the band is made evident by a distinct shading on the violet side of the first chlorophyll band, of about half the intensity of that band; the reason why it is now visible is because the band due to true chlorophyll is shifted more towards the red end in carbon disulphide as compared with alcohol, whilst the position of the other band remains almost constant in the two solvents.

The facts related make it quite certain that crude leaf extracts of higher plants contain two green colouring matters, of which one is the true chlorophyll, with all its well known properties, the other, present in considerably smaller quantities, also producing an absorption of certain red rays. Whether these two colouring matters are chemically allied or whether they are both necessary for performing the assimilating function is impossible to say at present, and although as a subject for future investigation the problem offers considerable difficulties, it deserves a thorough study.

As true chlorophyll differs in its solubility in alcohol and carbon disulphide from this new green colouring matter and the members of the xanthophyll group, we are able to obtain it in a comparative state of purity. Taking, as before, equal volumes of the crude extract (prepared with 82 per cent. methylated alcohol) and pure carbon disulphide and shaking the mixture well, the disulphide will subside, having taken up the major portion of the chlorophyll together with some of the new green colouring matter and a considerable portion of the xanthophylls. The chlorophyll, being the most soluble, is therefore present in a greater relative quantity than in the original extract. If this carbon disulphide solution is now shaken up with successive equal volumes of methylated spirit, the colouring matters are taken up again by the spirit in several fractions, but in different relative proportions, depen-

dent upon their solubility. The greater portion of the xanthophylls and the new green colouring matter, being more soluble in alcohol than true chlorophyll, will be contained in the first few fractions, and the later spirit fractions will consequently contain the chlorophyll in a relatively excessive quantity, although a considerable quantity will have been lost in the process. That these other colouring matters have been nearly, if not entirely, removed, can be proved by spectroscopically examining the later spirit fractions in carbon disulphide, water being added to them, which precipitates the dissolved disulphide, carrying along with it the chlorophyll.

It will now be found that the band in the red, due to the new green colouring matter, is absent, and there is also no indication of the band in the green, situated on the less refrangible side of the F line, which we have shown indicates the presence of the colouring matters of the xanthophyll group. This solution of purified chlorophyll in carbon disulphide is as green as the original alcoholic extract; it can be evaporated to dryness without change, and the residue, dissolved in alcohol, has exactly the spectroscopic properties of the crude alcoholic extracts already discussed, its spectrum in carbon disulphide and in alcohol being identical, with the exception that in the former solvent the bands are shifted a little towards the red end.

It now remains to determine to what extent, if at all, the product in question contains colourless impurities. We hope to be able to answer this question shortly.

### 3. ACTION OF BROMINE UPON PHYLLOPORPHYRIN AND HÆMATOPORPHYRIN.

¶ It is well known that the chemical and optical properties of phylloporphyrin, a derivative of chlorophyll, and of hæmatoporphyrin, a derivative of hæmoglobin, are very similar, facts which point to a close relationship of the two substances (E. Schunck and Marchlewski, *Proc. Roy. Soc.*, 1896, 59, 233). The study of the colourless oxidation products of both, which will be published in due course, seems to give a further proof of the correctness of this assumption. The present note deals with a reaction, to which is due a chemical change of phylloporphyrin and hæmatoporphyrin, not leading, however, to a complete decomposition of the chromophoric groups.

It has been shown by Arnold, in an interesting paper entitled "Ein Beitrag zur Spectroscopie des Blutes" (*Centrabl. med. Wissens.*, 1899, 465), that bromine, acting on the sulphate of so-called hæmatoporphyrin anhydride, causes a change in the original colour, which, being at first red with a bluish tint, becomes violet, and finally a dirty green. At the same time, very interesting changes in the absorption spectrum may be observed. The final product of the action of bromine on the

sulphate of hæmatoporphyrin anhydride, dissolved in a mixture of alcohol and chloroform, shows, according to Arnold, a spectrum with four absorption bands, the positions of which he gives as follows:

Band 1. $\lambda$ 650—615	Band 3. $\lambda$ 538—526
„ 2. $\lambda$ 592—578	„ 4. $\lambda$ 512—488

The first and fourth bands are very dark and broad, whilst the second and third are very faint and comparatively narrow. Under the influence of hydrochloric acid, the spectrum undergoes another change. The colour becomes pure green, and the spectrum consists of a single band in the red.

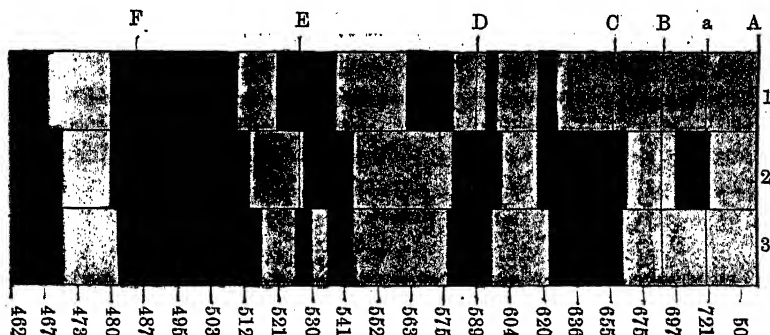
We have repeated Arnold's reaction, using, however, hæmatoporphyrin, prepared by the method given by Nencki and Sieber (*Monatsh.*, 1888, 9, 115), and compared the results with those obtained by the action of bromine on phylloporphyrin, prepared according to the well known method of heating phyllotaonin with alcoholic potash or soda to a high temperature in sealed tubes. The action takes place very gradually, as has been shown already by Arnold. We will first describe the final result, obtained by using a slight excess of bromine, and then the gradual changes observed under the influence of gradually increasing quantities of bromine.

Phylloporphyrin and hæmatoporphyrin dissolved in absolute alcohol give, on being treated with a sufficient quantity of bromine, olive-green solutions of somewhat different shades, the phylloporphyrin showing a slight violet tinge. The spectroscopic properties of the substances obtained may be seen from the accompanying plate, and in order to be able to appreciate the great change produced by the action of bromine, the spectrum of phylloporphyrin has also been inserted. The position of the bands, expressed in wave-lengths, may be ascertained by means of the annexed scale (p. 1093).

A comparison of the spectra will show first of all that the changes produced by bromine in the phylloporphyrin and hæmatoporphyrin spectra are, on the whole, very similar, but that at the same time certain important differences do exist. We notice that the "bromophylloporphyrin" shows a band in the extreme red which is absent in the case of "bromohæmatoporphyrin," and that the fourth band of the former corresponds to a double band in the latter. With the exception of the band in the extreme red in the case of the "bromophylloporphyrin," however, the spectra of both are much alike, a fact which points, we think, with certainty to a near relationship between phylloporphyrin and hæmatoporphyrin.

As regards the gradual changes of the spectrum under the influence of gradually increasing quantities of bromine, the following facts may be mentioned. If bromine solution be added to a phylloporphyrin

solution in alcohol, which is so far diluted (as depicted in the plate) that the second band in the orange close to the first band is invisible, a change will be noticed at once under the influence of the first drop. Two very faint bands appear in the red, the first phylloporphyrin band becomes fainter, the third and sixth shift somewhat towards the red, and a shading appears behind the fifth band. The second drop of bromine water produces further changes. Of the two bands in the red, the more refrangible becomes broader and darker, and the double band of phylloporphyrin shows signs of becoming a triple band. The third and fourth drops of bromine water cause the appearance of a faint band in the extreme red, the two bands in the red unite into a single one, which appears much broader



*Explanation of Plate.*

1. *Phylloporphyrin in alcohol.*
2. *Bromophylloporphyrin in alcohol.*
3. *Bromohæmatoporphylin in alcohol.*

and extends close to the first phylloporphyrin band. The triple band beyond the D line becomes more pronounced, whilst the sixth band is moved still further towards the red end of the spectrum. The fifth drop of bromine water causes the band in the extreme red to appear still darker, the two united bands in the red become still broader and cover now the space previously occupied by the first phylloporphyrin band, and the triple band near D disappears and is replaced by a single band. The sixth drop produces finally the spectrum given in the drawing. It will therefore be seen that the seventh band of phylloporphyrin is altered only to a very slight extent; it extends a little towards the red and becomes possibly slightly less intense. Very similar changes are noticed in the case of hæmatoporphylin, but there is no trace of a band in the extreme red, and the sixth hæmatoporphylin band is replaced by two faint ones in a somewhat different position.

As regards the changes of colour of the solutions, we have noticed exactly what is stated by Arnold about the sulphate of hæmatoporphyrin anhydride, namely, that the original red colour of the solutions changes to violet, and finally to olive-green. When hydrochloric acid is added to the olive-green solutions, a further change is noticed, the solutions become reddish-violet and exhibit a spectrum composed of several bands which, with the exception of the one in the red, are not well defined. It is rather difficult to say whether the spectrum, as depicted in the plate, really represents the final product of the action of bromine on phylloporphyrin and hæmatoporphyrin. We are inclined to think that it does, because further additions of bromine at first do not cause any appreciable change, whilst still larger quantities evidently destroy the products formed, for the fainter bands gradually fade away and the dark ones become gradually narrower.

The study of the changes of the acid solution of phylloporphyrin and hæmatoporphyrin under the influence of bromine is perhaps even more interesting than in the case of the free bases. The acid solutions exhibit, as is well known, only three bands, situated on either side of the D line, and consequently the gradual formation of the "bromophylloporphyrin" and "bromohæmatoporphyrin" spectra is particularly striking. The final products obtained possess a colour difficult to define, being of a reddish-brownish yellow, but the spectra are very much like those obtained with the neutral solutions, except that the bands are narrower and that the hæmatoporphyrin solution exhibits only four bands. It seems that the action of bromine on these substances, in presence of even a slight excess of acid, is more energetic than in the case of neutral solutions.

As regards the chemical nature of the products formed in Arnold's reaction, we do not intend for the present to express any definite opinion. It would seem that the changes observed are not due to oxidation, for concentrated nitric acid, when acting upon phylloporphyrin or hæmatoporphyrin, yields the same or analogous colour reactions as bromine, but the spectra of the solutions are quite different from those obtained when bromine is used, being composed of two bands only, situated in the green and yellow.

### XCVIII.—*Sulvanite, a New Mineral.*

By G. A. GOYDER.

This mineral was found in considerable quantity in some ore from a mine, not yet named, near the Burra in South Australia. It appears to afford the first recorded instance of a sulphide mineral containing vanadium as one of its principal constituents.

From the first analysis made, the composition appeared to be that of a sulphovanadate of copper,  $3\text{Cu}_2\text{S}, \text{V}_2\text{S}_5$ , mixed with chalcocite; a paper describing the mineral and giving this as a provisional structure, was read before the Royal Society of South Australia at Adelaide on June 5th.

On further examination, it was found that the sulvanite is so intimately penetrated by malachite and other oxidised minerals as to require fine comminution and digestion with dilute or weak acids before these oxidised portions can be removed.

Two samples, appearing nearly pure, were therefore finely ground, levigated and treated, one with cold dilute hydrochloric acid (1:1) and the other with 30 per cent. acetic acid heated on the water-bath; there was considerable evolution of carbon dioxide in each case, and much copper was dissolved. The washed and dried powders yielded the following figures on analysis, A having been treated with hydrochloric acid and B with acetic acid:—

	Cu.	V.	S.	$\text{SiO}_2$ .	
A .....	47.98	12.53	32.54	4.97	0.42
B .....	48.95	12.68	30.80	5.72	1.53

From these analyses, it appears that the mineral consists of sulphovanadate of copper,  $3\text{Cu}_2\text{S}, \text{V}_2\text{S}_5$ , and a table follows showing the composition of A and B after deducting the silica and iron, together with the calculated analysis of  $3\text{Cu}_2\text{S}, \text{V}_2\text{S}_5$ :

	Cu.	V.	S.
A .....	51.57	13.46	34.97
$3\text{Cu}_2\text{S}, \text{V}_2\text{S}_5$ (calc.).....	51.50	13.88	34.62
B.....	52.96	13.72	33.32

In these analyses, the sulphur is a little high in A from a slight decomposition of the sulphide by the action of hydrochloric acid, whilst in B the copper is high owing to the acetic acid having failed to remove all the oxidised copper minerals.

On heating a picked and apparently pure specimen in a closed tube before the blowpipe, a ring of sulphur was deposited on the cool surface of the tube, indicating the presence of vanadium pentasulphide,  $\text{V}_2\text{S}_5$ , or cupric sulphide; a previous test on a less pure fragment had given no sulphur, but another portion of this same fragment was found to contain only 8 per cent. of sulphur, which explains the discrepancy.

Physical properties of the mineral:—Massive, lustre metallic to sub-metallic, colour bronze-yellow, streak nearly black, hardness 3.5, sp. gr. 4.0. No crystalline form could be detected in the specimens examined, and this, with the presence of oxidised minerals, renders

the physical properties rather vague. Two specimens had the sp. gr. of 3.94 and 3.82, and the first, after deducting the effect of 5 per cent. of silica, gave the sp. gr. as 4.03; as malachite has the same sp. gr., its presence does not affect the result.

The associated minerals are malachite, azurite, quartz, vanadium ochre, gypsum, and calcite, with probably some copper vanadate, although none of this has, so far, been separated for identification.

NOTE.—In separating sulphuric acid from vanadium in hydrochloric acid solution, the vanadium should be first reduced from vanadium pentoxide,  $V_2O_5$ , to vanadium tetroxide,  $V_2O_4$ , otherwise the barium sulphate is contaminated with vanadic acid or barium vanadate, from which it cannot be freed by treatment with acids, whereas when first reduced, none or only negligible traces are carried down.

If solution has been preceded by fusion with sodium hydrogen carbonate and potassium nitrate, the nitrite present suffices for the reduction, otherwise the acid solution is boiled with a little alcohol until it is of a pure blue colour. The vanadium tetroxide is oxidised by bromine prior to precipitation as barium vanadate.

SOUTH AUSTRALIAN SCHOOL OF MINES AND INDUSTRIES,  
ADELAIDE.

## XCIX.—*Acetyl and Phenacetyl Derivatives of Diethyl d-Tartrate.*

By JOHN McCRAE and T. S. PATTERSON.

AMONG other questions concerning the relation of isomerism to optical activity, arises that of the comparative influence of the phenacetyl and toluyll groups on the rotatory power of optically active compounds into which they may be introduced. According to the hypothesis of Guye and Crum Brown, the phenacetyl group ought in this respect to resemble the isomeric toluyll group, whilst, on the other hand, from chemical analogy, it would rather be expected to resemble the acetyl group—as Frankland has pointed out (Trans., 1893, 63, 535)—or perhaps still more some other substituted acetyl group, for example, chloroacetyl.

Recent work has shown fairly clearly that the second of these two assumptions is confirmed by the facts. The results in the case of the glycerate series are shown in the following table (compare MacGregor and MacGregor, Trans., 1896, 69, 104; Frankland and



Patterson, Trans., 1898, 73, 181; Frankland and Aston, Trans., 1899, 75, 493):

Methyl glycerate .....	$[\alpha]_D^{20} = -4.80^{\circ}$	$[M]_D^{20} = -5.76^{\circ}$
„ di- <i>o</i> -toluylglycerate ...	„ = +20.2	„ = +71.9
„ „ <i>m</i> -toluylglycerate ..	„ = +26.4	„ = +94.0
„ „ <i>p</i> -toluylglycerate...	„ = +41.2	„ = +146.7
„ diphenacetyl-glycerate..	„ = -15.8	„ = -56.5
„ diacetyl-glycerate .....	$[\alpha]_D^{15} = -12.0$	$[M]_D^{15} = -24.6$
„ di-monochloroacetyl- glycerate .....	„ = -12.9	„ = -36.1
„ di-dichloroacetyl-glycerate	„ = -13.9	„ = -47.7
„ di-trichloroacetyl-glycerate	„ = -14.2	„ = -58.3

The introduction, therefore, of any of the acetyl groups into the methyl glycerate molecule alters the rotation in the positive direction, the influence of the toluyl groups being just the opposite.

Only two other series are known, so far as we are aware, in which a similar comparison can be instituted, the first being that of the menthyl esters, for which Tschügäeff (*Ber.*, 1898, 31, 360, 1778) gives the following:

Menthol .....	$[\alpha]_D = -50.0^{\circ}$	$[M]_D = -78.0^{\circ}$
Menthyl <i>o</i> -toluate .....	„ = -84.4	„ = -231.3
„ „ <i>m</i> -toluate .....	„ = -87.9	„ = -241.0
„ „ <i>p</i> -toluate .....	„ = -92.1	„ = -252.5
„ „ phenacetate .....	„ = -69.6	„ = -190.7
„ „ acetate .....	„ = -79.4	„ = -157.3

In this case, however, the difference in the effect of the phenacetyl and toluyl groups can scarcely be said to be so marked.

The third series which can be adduced is that of the diethyl diacetyltartrates, where we find a behaviour seemingly closely analogous to that of the glycerates. The diphenacetyl and diacetyl derivatives, previously prepared by Freundler, have been re-examined for the object of this investigation.

In the series of diethyl monoacetyltartrates, only diethyl mono-trichloroacetyltartrate (Frankland and Patterson, *loc. cit.*), diethyl monochloroacetyltartrate (Frankland and Turnbull, Trans., 1898, 73, 204), and the diethyl monotoluyltartrates (Frankland and McCrae, Trans., 1898, 73, 307) are known, and the object of the present investigation is to fill up the existing gaps and connect together the data for the diethyl mono- and di-acetyl-, -chloroacetyl-, -phenacetyl-, and -toluyl-tartrates.

## EXPERIMENTAL.

*Diethyl Diacetyltartrate.*

This substance was prepared from pure diethyl tartrate having the specific rotation  $+7.76^\circ$  at  $20^\circ$ , by boiling for some time under an inverted condenser with excess of acetic anhydride. The excess of anhydride was distilled off, and the residue, when cold, poured into water, when it almost immediately solidified. It was collected and recrystallised from aqueous alcohol, from which it separated in prisms melting at  $67-68^\circ$ .

The rotation of this product at  $100^\circ$  was found to be  $6.59^\circ$  in a 100 mm. tube.

The compound was then distilled under diminished pressure (about 15 mm.) and separated into two fractions. It boiled at  $170^\circ$ . The rotation of the second fraction was determined at various temperatures with the following results:

*Length of polarimeter tube, 66.04 mm.*

Temp.	Observed rotation.	Density.	$[\alpha]_D$ .	$[M]_D$ .	$[\delta]_D$ .
$100^\circ$	$4.49^\circ$	1.0793	$+6.30^\circ$	$+18.26^\circ$	$+43.87^\circ$
86.7	4.04	1.0928	5.60	16.24	39.31
78.2	3.78	1.1012	5.20	15.08	36.69
71.3	3.60	1.1086	4.92	14.27	34.86
67.6	3.49	1.1120	4.75	13.77	33.76
56.8	3.24	1.1229	4.37	12.67	31.24

It was not found possible to continue the observations to lower temperatures as the substance, cooled slowly in the polarimeter jacket, solidified a little below  $56^\circ$ .

The densities actually observed were:

$d_{98.5^\circ/4^\circ} = 1.0810$	$d_{70.7^\circ/4^\circ} = 1.1092$
$d_{81.2^\circ/4^\circ} = 1.0979$	$d_{65.5^\circ/4^\circ} = 1.1146$

The rotation of this substance has already been examined by Freundler (*Ann. Chim. Phys.*, 1894, [vii], 3, 454), who found for the observed rotation at  $25^\circ$  ( $l=1$  dm.) the value  $+5^\circ$ . The density was not determined. This number, judging from our results, is probably too high, which may be due to admixture with diethyl tartrate or diethyl monoacetyltartrate, both of which are liquid and of higher rotation.

*Diethyl Monoacetyltartrate.*

In order to prepare this substance, 90 grams of diethyl tartrate were dissolved in 200 grams of benzene and 34 grams of acetyl chloride were added in instalments of 5 c.c. daily. After the addition of each instalment, the solution was boiled on the water-bath during the rest of the day. When the reaction was over, the benzene was distilled off as far as possible from a water-bath and the rest removed by distillation in a vacuum. A few drops of tartrate were removed along with the benzene and the main fraction collected. The product of the reaction boiled between  $167^{\circ}$  and  $169^{\circ}$  under 15 mm. pressure (temp. of oil-bath,  $215-220^{\circ}$ ) and 94 grams were obtained.

A small portion of this was shaken up with water to remove diethyl tartrate. Most of it quickly went into solution, but left behind a residue which immediately solidified. This was diethyl diacetyltartrate, since the melting point after recrystallisation from aqueous alcohol was found to be  $67^{\circ}$ . Therefore, either diethyl monoacetyltartrate had not been formed or that substance is easily soluble in water, contrary to the statement of Perkin (this Journ., 1867, 20, 138), who prepared it by heating diethyl tartrate with acetyl chloride in theoretical quantity in a sealed tube.

In order to remove the diacetyltartrate which had been formed, the whole product was shaken up with water, and the resulting solid collected. According to an experiment made with another preparation at this stage, in which 1 gram of solid residue was obtained from 5 grams of substance, about 20 per cent. of the product consisted of diethyl diacetyltartrate, in spite of the precautions taken to prevent its formation. Sodium carbonate solution was added to the filtrate, which was then shaken for a short time (a previous experiment having shown that prolonged action of sodium carbonate can completely destroy the monoacetyl compound), and then extracted with ether. The ethereal solution was filtered, the ether distilled off, and the residue fractionated in a vacuum.

The colourless, viscid liquid thus obtained was examined in the polarimeter in a 100 mm. tube, and gave the rotations:

At $8^{\circ}$ .	$14.6^{\circ}$ .	$19.7^{\circ}$ .
+ $10.23^{\circ}$	+ $10.80^{\circ}$	+ $11.30^{\circ}$

the corresponding rotations for diethyl tartrate being

+ $7.80^{\circ}$	+ $8.7^{\circ}$	+ $9.35^{\circ}$
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Another preparation made in the same way had a rotation at  $14.8^{\circ}$  of +  $10.89^{\circ}$  in a 100 mm. tube.

Apparently, therefore, the best method of preparing this substance is treatment of diethyl tartrate in a large quantity of an indifferent solvent with the calculated quantity (or less) of acetyl chloride. The product on distillation gives a mixture of diethyl tartrate, diethyl monoacetyltartrate, and diethyl diacetyltartrate, and these three compounds cannot be separated by distillation. Diethyl tartrate, however, is miscible in all proportions with water, and, at any rate for the most part, can be removed by shaking with a *small* quantity of water. The remainder should then be again shaken with water and this operation repeated until a solid residue is left. In this way, diethyl monoacetyltartrate is obtained in solution. It is fairly easily soluble in water and can be extracted by ether, chloroform, benzene, &c., and distilled.

A third preparation was made as described. The diethyl monoacetyl tartrate was extracted with chloroform, the solution dried with calcium chloride, and the chloroform mostly distilled off. The residue was heated for some time in an air-bath at 100°, then allowed to stand in a vacuum until the smell of chloroform was gone. The pale yellow liquid which remained had a rotation of 10·50° in a 100 mm. tube at 17·5°. This was then distilled in a vacuum and the rotation of the middle fraction examined at different temperatures, with the following results:

Temp.	rotation.	Density.	$[\alpha]_D$ .	$[M]_D$ .	$[\delta]_D$ .
15°	10·71°	1·1859	+9·03°	+22·40°	+63·56°
18·1	10·89	1·1828	9·21	22·84	64·70
20·7	11·05	1·1800	9·36	23·21	65·70
31·2	11·60	1·1694	9·92	24·60	69·19,
50·3	12·55	1·1500	10·91	27·06	75·24
56·9	12·86	1·1436	11·25	27·90	77·29
67·4	13·36	1·1329	11·80	29·26	80·54
77·6	13·88	1·1224	12·37	30·68	83·94
86·4	14·30	1·1135	12·84	31·84	86·68
99·1	14·83	1·1008	13·47	33·48	90·14

The densities actually observed were:

$$d_{20\cdot4/4^\circ} = 1\cdot1805$$

$$d_{52\cdot2/4^\circ} = 1\cdot1481$$

$$d_{34\cdot9/4^\circ} = 1\cdot1656$$

$$d_{71/4^\circ} = 1\cdot1292$$

Twenty grams of the substance, whose rotation had thus been determined, were shaken with water; most of it went into solution, however, some solid residue behind. This was collected, and

when dry weighed 0.7 gram, showing that the substance had contained about 4 per cent. of diethyl diacetyltartrate. It is probable also that the substance contained a small proportion of diethyl tartrate, and the presence of these substances may be due either to the inadequacy of the means of purification adopted, or perhaps to a slight decomposition of the monoacetyl compound into tartrate and diacetyltartrate on distillation. To free the substance completely from these impurities is evidently a matter of considerable difficulty, inasmuch as by several repetitions of the method used and in several preparations the rotation remained practically constant. The quantity of admixed substance, however, is not great, and both impurities would lower the rotation, so that the true value of the rotation of the monoacetyltartrate should be a little higher than that which we have found.

Assuming that the influence of the impurities on the rotation is purely additive and that there was 5 per cent of each present, then  $[\alpha]_D^{20}$  of the pure substance would be approximately

$$\frac{100}{90} \left( 9.30 - \frac{5}{100} \times 7.66 - \frac{5}{100} \times 2.55 \right) = 9.76^\circ.$$

Since the percentages of carbon and hydrogen in the monoacetyl compound and in the impurities do not differ to any great extent, an ultimate analysis would not throw any light on the composition of the specimen examined.

#### *Diethyl Diphenacetyltartrate.*

16.5 grams of diethyl tartrate were added very slowly to 46 grams of phenacetyl chloride heated in an oil-bath at 120°. After all the ester had been added, the heating was continued until the evolution of hydrogen chloride had ceased, then finally the temperature of the bath was raised to 140° for 20 minutes.

In one case, the excess of acid chloride was distilled off under diminished pressure, and the residue shaken up with water. It was subsequently found that the diphenacetyltartrate decomposes when strongly heated, and consequently in the succeeding experiments the acid chloride was decomposed with water and not distilled off. The product was shaken with about 200 c.c. of water for some time, and, after separation, the oil was shaken with a solution of sodium carbonate, then dissolved in ether, and shaken on a machine for 6 hours with a fairly concentrated solution of sodium carbonate. The ethereal solution was washed well with water and then dried for a few minutes over ignited potassium carbonate. The ether was evaporated off and the yellowish, viscid residue dried in a vacuum

over sulphuric acid. The rotation of this substance at  $18^{\circ}$  in a 66.04 mm. tube was  $13^{\circ}$ . Attempts to distil it in a vacuum showed that it is only very slightly volatile without decomposition. At a pressure of 7 mm. (obtained by a Barr and Stroud mercury pump), a very little substance distilled at  $270^{\circ}$ , but much decomposition occurred, and the distillate was deeply coloured.

The liquid in one preparation was fractionally dissolved by, and separated from, light petroleum, and then had a rotation of  $20.5^{\circ}$  in a 100 mm. tube at  $19.25^{\circ}$ , equivalent to  $13.54^{\circ}$  in a 66.04 mm. tube. In another case, it was dissolved in ether and shaken with animal charcoal. After filtering, the ethereal solution was shaken with sodium carbonate solution and treated as before. The residue then had a rotation of  $13.93^{\circ}$  in a 66.04 mm. tube at  $15^{\circ}$ . A slow current of air was aspirated through the liquid in a vacuum, as recommended by Freundler (*loc. cit.*, 475). After this treatment, the rotation had slightly increased to  $13.90^{\circ}$  in a 66.04 mm. tube at  $20.2^{\circ}$  (this is an increase because the rotation decreases with rise of temperature).

Another preparation of the substance led to practically the same rotation, and this may be taken as evidence of the purity of the products.

Freundler (*loc. cit.*) has already examined this compound: he finds that at  $19^{\circ}$  in a 50 mm. tube it has the rotation  $8^{\circ}59'$ , and as its density at  $19^{\circ}$  is 1.174,  $[\alpha]_D^{19}$  is  $15.3^{\circ}$ . From our observations, we calculate that in a 50 mm. tube at  $20^{\circ}$  our preparation would have rotation  $10^{\circ}31'$ .

It has been found extremely difficult to rid the viscid liquid entirely of phenacetyl chloride or phenacetic acid, and possibly the explanation of the difference in the results which Freundler and we have obtained is due to this circumstance.

On analysis:

0.2354 gave 0.5606  $\text{CO}_2$  and 0.1250  $\text{H}_2\text{O}$ . C=64.96; H=5.90.

$\text{C}_{24}\text{H}_{26}\text{O}_8$  requires C=65.16; H=5.88 per cent.

The following density determinations were made:

$d\ 15^{\circ}/4^{\circ}=1.1793$ ;  $d\ 34.8^{\circ}/4^{\circ}=1.1603$ ;  $d\ 55^{\circ}/4^{\circ}=1.1424$ ;  
 $d\ 70^{\circ}/4^{\circ}=1.1276$ ;  $d\ 98^{\circ}/4^{\circ}=1.1024$ .

The rotation was determined at different temperatures, and the following results were obtained:

Temp.	rotation.	Density.	$[\alpha]_D$ .	$[M]_D$ .	$[\delta]_D$ .
12.5°	15.05°	1.1820	+19.28°	+85.22°	+164.2°
20.2	13.90	1.1748	17.91	79.16	151.9
34.5	12.15	1.1613	15.84	70.01	133.3
43.5	11.17	1.1530	14.67	64.84	122.9
52	10.06	1.1447	13.31	58.83	110.9
60.5	9.33	1.1371	12.42	54.89	103.1
73.7	8.27	1.1248	11.13	49.19	91.7
85	7.45	1.1146	10.12	44.73	82.9
99.5	6.57	1.1016	9.03	39.91	73.4

*Diethyl Monophenacetyl tartrate.*

Fifteen grams of phenacetyl chloride were added, drop by drop, to 75 grams of diethyl tartrate heated on the water-bath. The addition must be made slowly, and it is essential to shake the mixture well after each drop has been added. After the apparent evolution of hydrogen chloride had ceased, the mixture was kept on the water-bath for 1 to 2 hours, and after cooling poured into water. The separated oil was well shaken with a solution of sodium carbonate, then dissolved in ether, and the solution, after being shaken on a machine for 6 hours with fresh sodium carbonate solution, was washed, dried, and evaporated. The residual oil, after drying in a vacuum over sulphuric acid, had a rotation of 27° in a 100 mm. tube at 18°. In this condition, the substance contains an appreciable quantity of the diphenacetyl compound, and if subjected to distillation in a vacuum, the distillate is impure and coloured by the decomposition products of the latter. In order to get rid of most of this impurity, it has been found that dissolution in, and separation from, light petroleum leads to a satisfactory result. The liquid was warmed with a quantity of light petroleum, insufficient to completely dissolve it. The solution was poured off from the undissolved portion, and, on cooling, an almost colourless oil separated out. This oil had a higher rotation than before, and after being several times treated in this manner, the rotation rose to 32.33° in a 100 mm. tube at 18°. The liquid was then distilled under 11 mm. pressure, and the part boiling at 225—230° had a rotation of 35.07° in a 100 mm. tube at 16°. After two further distillations in a vacuum, the rotation rose to 35.90° in the same tube at 21°, and this was found to be constant on redistilling the substance.

This constant rotation has been found for different prepara-

tions, and shows that the substance had been obtained in a pure state.

The monophenacetyl compound is a viscid, colourless oil—not nearly so viscid, however, as the diphenacetyl derivative—and did not solidify in a freezing mixture of solid carbon dioxide and ether. The isomeric toluyll compounds have been obtained in the solid state (Frankland and McCrae, *loc. cit.*), but, whereas they decompose on distillation, the phenacetyl compound can be distilled. It has been mentioned that it is not advisable to distil the monophenacetyl compound until it has been obtained in a state of comparative purity; possibly the decomposition noticed in the attempts to distil the monotoluyll compounds was due to impurities, although the two cases are not quite analogous, since Frankland and Wharton have shown that the ditoluylltartrates are volatile, and we have found that diethyl diphenacetyltartrate is only very slightly so.

On analysis :

0.1613 gave 0.3505  $\text{CO}_2$  and 0.0875  $\text{H}_2\text{O}$ . C = 59.26 ; H = 6.07.

$\text{C}_{16}\text{H}_{20}\text{O}_7$  requires C = 59.26 ; H = 6.17 per cent.

The following density determinations were made :

$d\ 36^\circ/4^\circ = 1.1721$	$d\ 80^\circ/4^\circ = 1.1304$
$d\ 59^\circ/4^\circ = 1.1504$	$d\ 93^\circ/4^\circ = 1.1153$

The rotation of the substance was determined at different temperatures, and the following results were obtained :

*Length of polarimeter tube, 30.5 mm.*

Temp.	Observed rotation.	Density.	$[\alpha]_D$ .	$[M]_D$ .	$[\delta]_D$ .
6.5°	11.60°	1.2000	+31.69°	+102.67°	+245.8°
21.5	10.95	1.1863	30.26	98.04	232.9
35	10.37	1.1726	29.00	93.96	221.5
39	10.17	1.1692	28.52	92.39	217.4
41.5	10.01	1.1669	28.12	91.11	214.1
50	9.63	1.1586	27.25	88.29	206.5
60.5	9.27	1.1484	26.47	85.76	199.3
72	8.88	1.1382	25.58	82.88	191.5
81.5	8.52	1.1282	24.76	80.22	184.3
88.5	8.32	1.1206	24.34	78.86	180.4
99.5	8.13	1.1100	24.02	77.82	176.8

*Molecular volumes at 15°.*

These have been calculated according to I. Traube's formula :

$$V_m = m \cdot 9C + n \cdot 1H + p \cdot 2.3O' + q \cdot 5.5O'' + 25.9 - r \cdot 13.2C_6H_6 \text{ ring.}$$



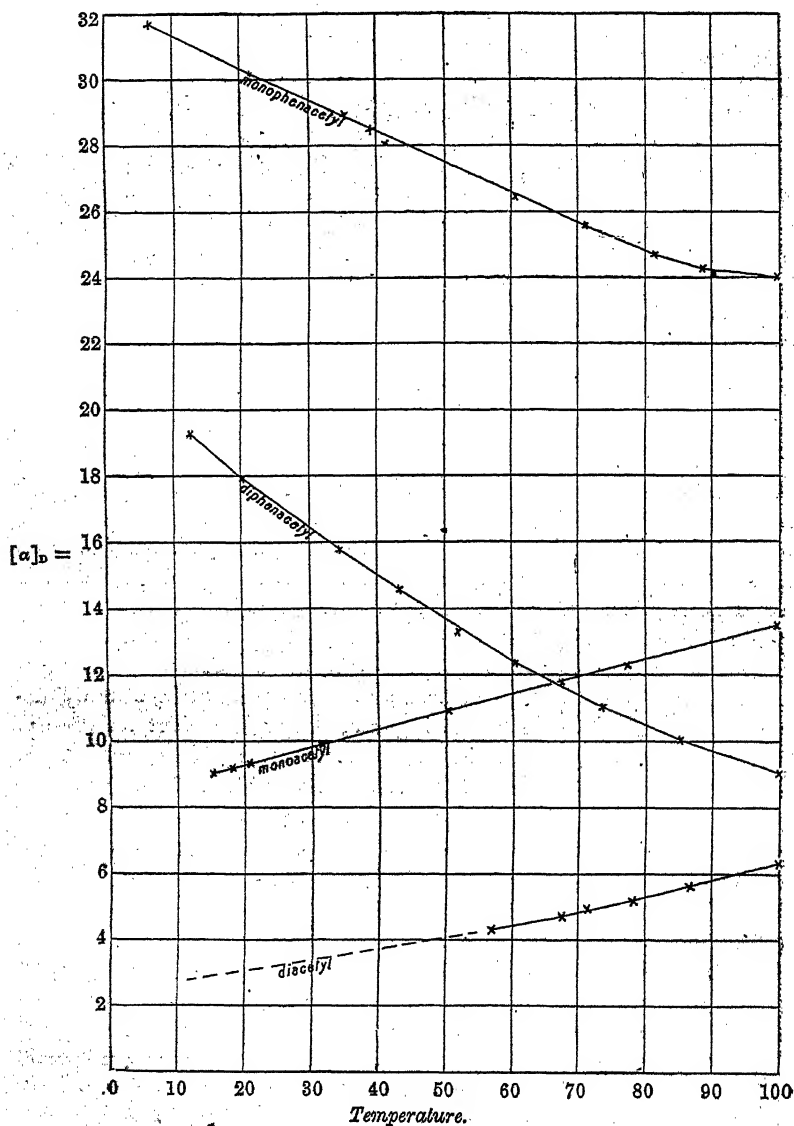
	Mol. wt. $d\ 15^{\circ}/4^{\circ}$ .	Experimental mol. vol. at 15°.	Calculated mol. vol. at 15°.
Diethyl diacetyltartrate .....	$\frac{290}{1.1673}$	248.4	244.5
„ monophenacetyltartrate	$\frac{324}{1.1920}$	271.8	268.4
„ diphenacetyltartrate ...	$\frac{442}{1.1793}$	374.8	374.9

In the case of the diphenacetyl derivative, the agreement between the experimental and calculated molecular volume is very satisfactory, and the numbers found for the diacetyl and monophenacetyl compounds do not point to any "association" of their molecules. The calculated value in the case of the monoacetyl compound is in close agreement with the theoretical (experimental, 209.1; calculated, 209.8), but has not been included in the table, as our preparation was not pure.

#### CONCLUSIONS.

The results which we have obtained in the examination of these compounds are plotted in Fig. I (p. 1106) in the form of curves, showing the variation of specific rotation with temperature. It will be seen, in the first place, that the rotations of the acetyl and phenacetyl derivatives behave quite differently, the former having a positive, and the latter a negative, coefficient, but this does not necessarily indicate some radical difference of properties of the substituting groups. These compounds may rather be regarded as extreme members of a series in which the temperature-coefficient, at first positive, gradually decreases, and ultimately becomes negative. The coefficient for diethyl di-monochloroacetyltartrate is, like that of diethyl diacetyltartrate, positive, whilst that of diethyl di-dichloroacetyltartrate is positive, but only very small (Frankland and Patterson, *loc. cit.*), and probably that of the di-trichloroacetyl compound, if it could be prepared, would be found to be negative, like that of the phenacetyl derivative.

It is noticeable that the coefficient of the monoacetyltartrate is greater than that of the diacetyl compound, this applying also to the phenacetyl derivatives, for the coefficient of the di-substituted compound is, in this case, more negative than that of the mono-substituted derivative, and we have, therefore, in the monoacyl series, the same regularity as before, namely, a considerable positive coefficient changing gradually on passing through acetyl, monochloroacetyl, trichloroacetyl (which has almost reached insensitiveness, but whose coefficient is slightly positive), to phenacetyl, whose coefficient is negative and large.

FIG. I.—*Influence of Temperature on the Specific Rotation of Mono- and Di-acetyl- and -phenacetyl-tartrates.*

With the data now available, a table can be drawn up of the molecular rotations of the diethyl monoacyltartrates as follows:

	$[M]_D^{20^\circ}$	$[M]_D^{100^\circ}$
Diethyl tartrate .....	+15.86°	+27.6°
„ monoacetyltartrate.....	23.1	33.5
„ mono-monochloroacetyltartrate	32.3	48.9
„ mono-trichloroacetyltartrate...	54.7	61.7
„ monophenacetyltartrate.....	98.5	77.8
„ monobenzoyltartrate .....	61.4	54.8
„ mono- <i>o</i> -toluyltartrate.....	38.2	35.3
„ mono- <i>m</i> -toluyltartrate .....	44.0	40.8
„ mono- <i>p</i> -toluyltartrate.....	63.5	51.2

So far, therefore, as qualitative effect on the rotation is concerned, the introduction of each of these radicles into the diethyl tartrate molecule is similar—the rotation is increased. This is also the case in the menthyl series quoted above, but from a quantitative point of view it is obvious from the figures in the table that the regularities observed in the glycerate and menthyl series are not found here, inasmuch as the toluy groups have a greater effect on the rotation than the acetyl, but a less effect than the phenacetyl radicles.

In relation to the variation of rotation with temperature, there is a distinct difference to be noticed in the behaviour of these substances. The temperature-coefficient in the case of the monoacetyl-, mono-monochloroacetyl-, and mono-trichloroacetyl-tartrates is, like that of diethyl tartrate itself, positive, whereas, with the others tabulated, it is negative. Of the latter, the greatest diminution of rotation with rise of temperature is shown by the phenacetyl compound, which, therefore, in this respect, shows a much greater divergence than even the toluy derivatives from the behaviour of the acetyl compound.

Passing now to the diacyl derivatives, we have the following data:

	$[M]_D^{20^\circ}$	$[M]_D^{100^\circ}$
Diethyl tartrate.....	+15.86°	+27.6°
„ diacetyltartrate.....	+9.9*	+18.3
„ di-monochloroacetyltartrate	+25.5	+39.4
„ di-dichloroacetyltartrate ...	+65.8	+68.9
„ diphenacetyltartrate.....	+79.2	+39.9
„ dibenzoyltartrate .....	-247.1	-251.6
„ di- <i>o</i> -toluyltartrate.....	-266.5	-241.9
„ di- <i>m</i> -toluyltartrate .....	-306.3	-281.7
„ di- <i>p</i> -toluyltartrate.....	-484.4*	-397.7

\* Calculated.

A comparison of the molecular rotations of the diacyl compounds shows, in the first place, a striking qualitative difference between the first four derivatives of diethyl tartrate and the last four in the table; a division into two classes thus seems to be indicated, as in the case of the glycerates already quoted. At the same time, however, the acetyl and phenacetyl radicles have a different quantitative effect, for the introduction of the two acetyl groups somewhat diminishes the positive rotation of diethyl tartrate, the two benzoyl\* and the two toluyl groups exert a very great influence in the same direction, whilst the two phenacetyl groups cause a slight increase in the positive rotation.

With regard to the effect of temperature, it will be noticed that in this series, the phenacetyl compound † has a negative temperature-coefficient but those of the toluyl and acetyl derivatives are positive. In the monoacyl series, it might be said that the phenacetyl and toluyl radicles have a similar function; exactly the opposite may be concluded in this diacyl series.

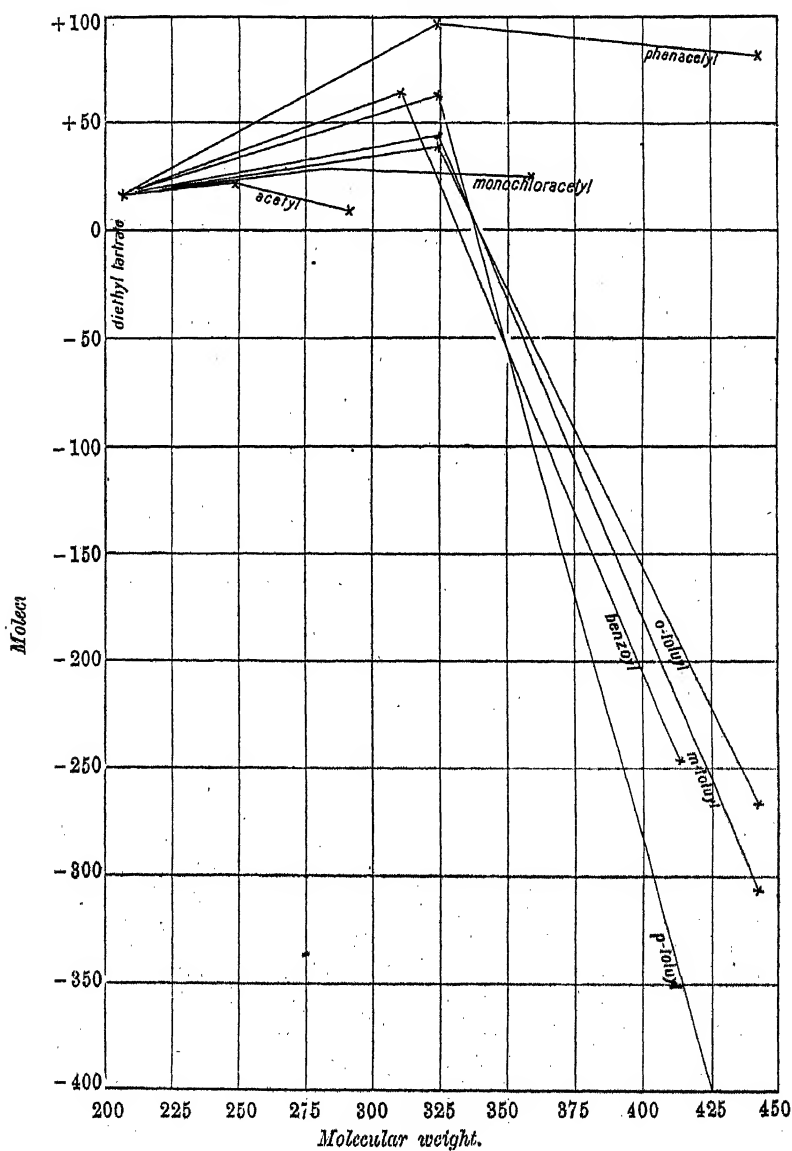
It would appear, therefore, that in one series of similar compounds the phenacetyl and toluyl derivatives behave alike, but in another differently, and that the data given seem as yet to be capable of no generalisation. This, however, is not the case, for, in fact, a much more comprehensive regularity than is at first sight apparent can be shown to exist. This is noticed if we compare the effect produced by the introduction of one acyl group into the diethyl tartrate molecule with that produced when two such groups are introduced. In every case so far examined, the rotation has been increased when one acyl is substituted for the hydrogen of one hydroxyl group, but when the hydrogen of the other hydroxyl is replaced by another acyl, then the positive rotation of the monoacyl derivative is diminished. The extent of this diminution varies greatly with the nature of the substituting acyl radicle; thus, with phenacetyl, the diminution is not so great as was the first increase, with acetyl the decrease is a trifle greater than the first increase, but with benzoyl and toluyl the diminution is so great that the diacyl compounds have a very high lævorotation. This regularity is clearly exhibited by the diagram (Fig. II, p. 1109) in which the abscissæ are taken proportional to the molecular weights of the compounds.‡ The lines in this table have

\* The benzoyl compounds have been introduced in the tables in order to show how they compare with the toluyl derivatives.

† This applies also to the benzoyl compound between the temperature limits 20° and 100°.

‡ The point for di-*p*-toluyltartrate falls outside the table (at -484° for molecular weight 448,) but the inclination of the line shown is correct.

FIG. II.—Comparison of the Molecular Rotations at 20° of Diethyl Mono- and Di-acyltartrates.



no direct meaning, they merely serve to connect the three points, but it is seen clearly by their resemblance—initial rise and subsequent fall—that these acyl groups exert a similar qualitative influence.

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LEEDS.

### C.—*Estimation of Atmospheric Carbon Dioxide.*

By JAMES WALKER.

WHEN atmospheric carbon dioxide is estimated by means of Pettenkofer's method in its ordinary form, the results are often irregular and almost invariably too high from absorption of carbon dioxide from expired air during the process of titration. Many modifications have been proposed for avoiding this and other sources of error. For an account of these and for valuable accurate original observations, reference may be made to the memoirs of Blochmann (*Annalen*, 1887, 237, 39) and of Letts and Blake (*Proc. Royal Dublin Soc.*, 1900, 9, 107).

The following modification, which I have used for some time, can be worked without any special appliances, and gives results which have an accuracy of 0.1 part in 10,000 under ordinary circumstances, whilst permitting the analysis of air containing any quantity of carbon dioxide from 0 to 40 volumes in 10,000 without any alteration in the mode of working.

The solutions employed are decinormal hydrochloric acid which has been exactly standardised, and a clear solution of baryta, the strength of which relatively to the hydrochloric acid is accurately known. The baryta solution is most conveniently made about 0.02 normal, and is kept in a stock bottle with a 50 c.c. burette attached, as described in Ostwald's *Physicochemical Measurements*, pp. 88 and 250.

The bottle in which the sample is collected is a clean, dry Winchester quart, the capacity of which has been previously determined. This bottle may either be furnished with a rubber stopper and tubes as described below, or with its own ground glass stopper covered with a very thin film of a stiff grease. In the latter case, immediately before the determination is to take place, the glass stopper is rapidly exchanged in the open air for a rubber stopper through which pass two glass tubes, about 7 mm. in diameter. The longer tube reaches almost to the bottom of the bottle; the shorter tube ends internally flush with the stopper. Both tubes project externally about 2 inches, and are provided with stopcocks at slightly different levels so as to permit of convenient manipulation. There is permanently attached to the upper end of the longer tube a piece of rubber tubing 1 inch in

length which serves to connect it with the jet of the baryta burette. This jet is best constructed of barometer tubing very slightly tapered and cut off square at the end. Fifty c.c. of baryta solution, which will suffice for 40 vols. of carbon dioxide in 10,000 vols. of air, are slowly run in with both stopcocks open. The rubber is then detached from the jet and compressed by the fingers in order to force the baryta solution which may remain in the tube down below the level of the stopcock. Both stopcocks are then closed, and the bottle, which is allowed to lie on its side, is agitated from time to time.

While the absorption of the carbon dioxide is in progress, an asbestos filter is prepared. The best form to use is a Soxhlet cuprous oxide tube, which is fitted into a filtering flask of about 200 c.c. capacity by means of a rubber stopper. A very small quantity of asbestos well teased out is pressed down over the capillary portion of the tube, the filter pump is then turned on, and several fills of distilled water run through the tube. When the pump is running at full speed, the water should flow from the filter tube in a continuous stream, but should only drop slowly when the suction is slight. After a little practice has been acquired, the preparation of a satisfactory filter only occupies a few minutes.

If the bottle has been repeatedly agitated, the absorption of the carbon dioxide may be regarded as complete in 15 minutes, and the filtration may take place. Ten c.c. of hydrochloric acid solution are introduced into the empty filtering flask by means of a pipette which is always used for the same purpose; the filter tube is fitted in, and the flask, resting on the sole of a retort stand, is clamped firmly by the neck. The bottle is now clamped in an inverted position on the same retort stand about 8 inches above the top of the filtering tube. Into this there is fitted a rubber stopper, through which passes a short glass tube, connection with the shorter tube of the bottle being completed by means of a piece of rubber tubing  $\frac{1}{8}$  inch in bore,  $\frac{3}{8}$  in diameter, and about 8 inches in length. The filter pump is now turned on, and the stopcock of the shorter tube slowly opened. The barium carbonate remains on the asbestos, and the clear baryta solution which passes through is at once neutralised by the hydrochloric acid. When all the liquid has been filtered, the pump is allowed to act for a few moments so as to partially exhaust the bottle. The stopcock of the shorter tube is then closed.

Meanwhile 100 c.c. of distilled water, which always contains carbon dioxide in solution (compare Letts and Blake, *loc. cit.*, 125; Walker and Cormack, this vol., 8, 11), is neutralised by adding to it phenolphthalein, a little barium chloride solution, and then baryta solution until an incipient pink colour is produced. Into this prepared wash-water, contained in a small beaker, the end of the longer tube is

dipped, and the stopcock opened. The bottle being partially exhausted, water flows up the tube into the interior. When 20—30 c.c. have entered, the stopcock is closed. The bottle is then unclamped, and thoroughly rinsed by rotating and shaking while in a horizontal position. After the bottle is replaced in the clamp, the stopcock of the shorter tube is opened, and the wash-water allowed to filter into the flask. This process of washing is twice repeated. At the third washing, the prepared water is not in general turned pink when the bottle has been rinsed, showing that no baryta remains. Air is now admitted and the flask detached. The contents may be titrated with the standard baryta solution directly in the flask, but I have found it more convenient to transfer them to a porcelain casserole before titration. When the point of neutralisation is almost reached, the flask is washed out with a portion of the nearly neutralised liquid, and the neutralisation then completed.

The mode of calculation may best be seen from the following example.

Ten c.c. of decinormal hydrochloric acid required 50·80 c.c. of the baryta solution for neutralisation. One c.c. of baryta solution therefore corresponded to 0·2205 c.c. of  $\text{CO}_2$  at N.T.P.

The capacity of the bottle used was 2650 c.c., and the temperature of collection  $15^\circ$ . Fifty c.c. of baryta were introduced into the bottle, so that the air remaining in the bottle was  $2650 - 50 = 2600$  c.c. After absorption of the carbon dioxide, the baryta was filtered and washed into 10 c.c. of decinormal HCl, which then required 4·50 c.c. of baryta for complete neutralisation. There were thus used altogether  $50\cdot00 + 4\cdot50 = 54\cdot50$  c.c. of baryta solution, 50·80 of which were neutralised by the hydrochloric acid, giving 3·70 as the remainder neutralised by the carbon dioxide contained in the air examined. For the proportion of carbon dioxide in the air we have then

$$\frac{3\cdot70 \times 0\cdot2205 \times 10540}{2600} = 3\cdot31 \text{ vols. } \text{CO}_2 \text{ in 10,000 vols.,}$$

10,540 being the volume occupied at  $15^\circ$  by 10,000 vols. air at  $0^\circ$ .

In order that a comparison of Pettenkofer's original process and the modified method may be effected, I give a few results in which both modes of analysis were adopted, the samples being collected simultaneously. For the Pettenkofer values I am indebted to Mr. John Foggie, who has had a very large experience of the method.

Pettenkofer's method.	Modified method.	Difference.
4·4	3·7	0·7
4·1	3·5	0·6
26·4	26·2	0·2



These numbers reproduce almost exactly the differences found by Haldane and Pembrey between the Pettenkofer bottle method and their own gravimetric method (*Phil. Mag.*, 1890, [v], 29, 306).

In order to test the modification directly, several blank experiments were made. The experimental bottle was filled with air perfectly free from carbon dioxide, and the whole process of estimation gone through exactly as above described. In three experiments, the quantities of carbon dioxide found were 0.09, 0.02, and 0.05 vol. in 10,000 vols. of air. Again, 1.89 c.c. of carbon dioxide measured at 19° and 761 mm., corresponding to 1.77 c.c. at N.T.P., were introduced into the vacuum bottle which was then filled with air free from carbon dioxide. The quantity of carbon dioxide found by analysis was 1.78 c.c. at N.T.P., the error being 0.04 vol. in 10,000 vols. of air.

It is thus apparent that the method under the above conditions gives results which have certainly an error amounting to less than 0.1 part in 10,000, whilst permitting estimations up to 40 vols. in 10,000. Greater accuracy could no doubt be obtained by using considerably more dilute solutions, but the range of the method would be thereby limited. It is possible, as Mr. Foggie showed in some special experiments, to work the process accurately in bottles of only 1 litre capacity, a great convenience when many samples have to be collected at a distance from the laboratory. In this case, it is expedient to use twentieth normal hydrochloric acid and hundredth normal baryta. The time occupied in the analysis of a sample is generally less than half an hour.

With respect to the action of baryta solution on glass or rubber, which has been proved by various experimenters to affect the titre of the solution, it may be said that the error due to this cause is negligible in the above mode of working, the time during which the baryta is in contact with the bottle being too short for appreciable action, at least in the case of bottles which have been previously used for the same purpose.

If, as sometimes happens when the air is collected in factories or workshops, the temperature of collection is greatly above the atmospheric or laboratory temperature, a correction must be made for the amount of carbon dioxide which enters with the atmospheric air when the pressure is adjusted by opening the bottle before analysis. This correction may easily be calculated on the assumption that the external air contains 3 vols. in 10,000, and only amounts to 0.1 vol. for 10° difference in temperature. The rapid substitution of the rubber stopper for the glass stopper does not appreciably affect the result, as the following example shows. Two samples were collected simultaneously, one bottle being provided with the rubber stopper and tubes, and the other with a glass stopper. The results of the analyses

were 13.00 and 12.93 respectively, the difference being 0.07 vol. in 10,000. I have also found that the samples may be safely left for 24 hours before analysis, whether a rubber or a glass stopper is used.

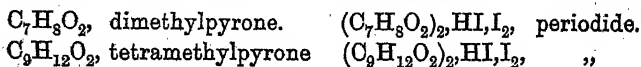
UNIVERSITY COLLEGE, DUNDEE.

### CI.—*Periodides of Substituted Oxonium Derivatives.*

By J. N. COLLIE, F.R.S., and B. D. STEELE, B.Sc. (Melbourne),  
1851 Exhibition Scholar.

THE property of forming salts with acids possessed by oxygen compounds, such as dimethylpyrone, trimethylpyrone, &c., has already been pointed out (Trans., 1899, 75, 510), and the similarity of these substituted "oxonium" compounds to the corresponding substituted ammonium compounds commented on. The present communication deals with the preparation and properties of some pyrone periodides. These compounds are crystalline substances, insoluble in water, and resembling in a marked degree the periodides of the pyridine bases.

During the investigation of the salts of tetramethylpyrone, it was noticed that when the solution of the iodide was allowed to evaporate in the air, brownish crystals slowly separated out, which were hardly soluble in water, and differed entirely from tetramethylpyrone iodide, which is a very soluble salt. The crystals gave off iodine when heated, also they were reconverted into dimethylpyrone when treated with soda. That the substance was a periodide seemed evident from its properties, as it resembled the insoluble periodides of such nitrogen bases as those of the pyridine series and the alkaloids. This idea was confirmed by the fact that when free iodine in a potassium iodide or hydriodic acid solution was added to a tetramethylpyrone salt, an immediate precipitate at once formed. These periodides were found to have the following constitution:

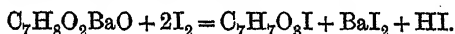


That substituted oxonium compounds form periodides in an exactly similar manner to substituted ammonium compounds is of some interest, as it affords evidence of the similarity of complex oxygen bases to the more complex alkaloidal bases.

The action of iodine on the salts that dimethylpyrone forms with strong bases, such as sodium and barium hydroxides, was also investi-

gated. The reaction, however, proceeds in a quite different manner, and the chief product is an oxidised iodine compound,  $(C_7H_7O_3I)$ , which, like the periodide, is almost insoluble in water.

The compound, however, is not an ordinary iodide, for it does not lose iodine even when dissolved and warmed in a solution of sodium hydroxide or ethoxide. Acids such as hydrochloric or sulphuric, however, at once liberate iodine from it. At present, we are unable to explain the rather remarkable properties of this iodine compound; it may, perhaps, be formed by the following reaction:



The hydriodic acid thus liberated would decompose a further quantity of the barium salt into barium iodide and dimethylpyrone.

#### EXPERIMENTAL.

##### *Dimethylpyrone Periodide, $(C_7H_8O_2)_2HI_2$ .*

This compound is formed as a crystalline, orange-red precipitate when a solution of iodine in hydriodic acid is added slowly to an acetic acid solution of dimethylpyrone. When first precipitated, it is practically pure, and after drying rapidly in a desiccator melts at  $112-114^\circ$  with decomposition and liberation of iodine. It may be crystallised from glacial acetic acid, and after crystallising three times its melting point is unchanged.

The compound is very unstable, losing iodine slowly if exposed to the air or in a desiccator, and very rapidly at  $60^\circ$ , whilst it is immediately decomposed by water, iodine being liberated. Part of the iodine, approaching two-thirds of the total, can be estimated by means of sodium thiosulphate. A large number of titrations of the free iodine were made, and it was found that in specimens that had been kept for some time the percentage of iodine, as found by titration with thiosulphate, was low, sinking to 35.5 per cent. and 32.8 per cent. Specimens that had been prepared and dried as rapidly as possible, gave  $I=37.8$  per cent. as the mean of six analyses, the amount of free iodine calculated for a substance of the formula  $(C_7H_8O_2)_2HI_2$  being 40.1 per cent.

In the estimation of total iodine by silver nitrate, it was also found necessary to use samples which had been recently prepared, otherwise the percentage of iodine was found to be low.

0.1797 contained 0.1080 total iodine.  $I=60.1$ .

0.2386       "       0.1437       "       "        $I=60.3$ .

0.2372 gave 0.2327  $CO_2$  and 0.0612  $H_2O$ .  $C=26.7$ ;  $H=2.8$ .

$C_{14}H_{17}O_4I_8$  requires  $C=26.6$ ;  $H=2.7$ ;  $I=60.4$  per cent.

*Tetramethylpyrone Periodide,  $(C_9H_{12}O_2)_2HI, I_2$ .*

This is thrown down in the same manner as the preceding compound when iodine dissolved in hydriodic acid is added to an acetic acid solution of tetramethylpyrone. When first precipitated, it is finely crystalline, and contains a variable amount of free iodine; this may be removed and the substance purified by crystallisation from glacial acetic acid. Thus crystallised, it occurs in dark olive-brown, lustrous forms, and, whilst undergoing decomposition with loss of iodine, is not so unstable as the corresponding dimethylpyrone derivative, although, like the latter, it is immediately decomposed with liberation of free iodine when added to water or dilute acids. It melts at 126—128° with decomposition. On analysis:

0.2962 contained 0.1052 free iodine.  $I = 35.5$ .

$(C_9H_{12}O_2)_2HI, I_2$  requires free iodine = 37.0.

0.1914 contained 0.1048 total iodine.  $I = 55.3$ .

0.1497       "       0.0826       "       "        $I = 55.1$ .

0.2934 gave 0.3373  $CO_2$  and 0.0980  $H_2O$ .  $C = 31.3$ ;  $H = 3.7$ .

$C_{18}H_{26}O_4I_3$  requires  $C = 31.4$ ;  $H = 3.6$ ;  $I = 55.5$  per cent.

*Action of Iodine on the Barium Salt of Dimethylpyrone.*

When the barium salt of dimethylpyrone, which, according to Feist (*Annalen*, 1890, 257, 253), has the composition  $C_7H_8O_2, BaO, 4H_2O$ , is suspended in alcohol, and iodine added, reaction takes place with development of heat, and the barium compound dissolves; all action ceases when 2 atoms of iodine have been added for each atom of barium present. On standing for about 5 minutes and cooling, a salt containing barium and iodine crystallises out in slender, silky needles. This is soluble in acetic acid, and from the solution a substance crystallises out containing iodine and no barium; this is soluble in and may be crystallised from alcohol, and then has a melting point of 110—111°.

A further yield of the same substance may be obtained from the alcoholic filtrate from the first crop of crystals (those containing barium) by largely diluting with water, when slender, needle-shaped crystals separate out, which, after recrystallisation from alcohol, melt at 110—111°.

The total yield of the substance is small, never reaching 50 per cent. of the theoretical, and since analyses prove it to be an oxidised compound, it is certain that the reaction which takes place is by no means a simple one.

In the residues are found considerable quantities of a volatile substance, probably iodoacetone, which attacks the eyes.

The substance, after recrystallisation from alcohol, was analysed, with the following results :

0.2461 gave 0.2834  $\text{CO}_2$  and 0.0606  $\text{H}_2\text{O}$ .  $\text{C} = 31.4$ ;  $\text{H} = 2.7$ .

0.2857 „ 0.3313  $\text{CO}_2$  „ 0.0700  $\text{H}_2\text{O}$ .  $\text{C} = 31.6$ ;  $\text{H} = 2.6$ .

0.1814 „ 0.1591  $\text{AgI}$ .  $\text{I} = 47.4$ .

$\text{C}_7\text{H}_7\text{O}_3\text{I}$  requires  $\text{C} = 31.6$ ;  $\text{H} = 2.6$ ;  $\text{I} = 47.7$  per cent.

The compound is soluble in acetic acid, alcohol, chloroform, or ether, and in alkaline solutions, but is decomposed by mineral acids. With ferric chloride, it gives a deep red precipitate. When first prepared, the crystals are white, rapidly becoming yellowish, the yellow colour deepening with age.

On exposure to sunlight or to bright, diffused daylight, iodine is liberated, the action being more marked if the specimen is moist, and once the action is started it proceeds slowly even in the dark. By the prolonged action of sunlight, the substance becomes pasty, and a compound is produced in very small quantities, which is insoluble in alcohol, but when crystallised from acetic acid is bright red in colour, and melts with somewhat violent decomposition at  $187-190^\circ$ ; it was, however, produced in too small quantities to examine properly.

When treated with nitric or sulphuric acid in the cold, iodine is liberated in considerable quantities, as is also the case on heating with strong hydrochloric acid. In one experiment, after boiling for some time with hydrochloric acid, a brown, amorphous substance was extracted, which could not be obtained in a crystalline condition, and was evidently a condensation product. Hydriodic acid gave the same result.

When boiled with a strong solution of sodium hydroxide or ammonia, solution takes place, but apparently no decomposition, as no volatile products could be detected, and nothing could be isolated from the residues, whilst on rendering the solution faintly acid, the original substance is precipitated. When boiled with an alcoholic solution of sodium ethoxide, solution takes place, but on diluting and neutralising, the original substance is recovered unchanged. Whilst it is insoluble in water, it dissolves readily on heating in solution of potassium iodide. It is also soluble in the cold in strong solutions of sodium carbonate and sodium hydrogen carbonate, and is precipitated unchanged on neutralising.

Attempts have been made without success to prepare an acetyl derivative.

*The Barium Compound.*—As already stated, the crystals which are first produced in the interaction of iodine and the barium salt of

dimethylpyrone contain barium. This substance, however, is not produced if in the preparation of the iodine compound a larger quantity of alcohol is employed and this is diluted with water before the barium compound has had time to crystallise out.

The barium compound is immediately decomposed by acetic acid, and is insoluble or very sparingly soluble in water or alcohol; it may, however, be crystallised from a large bulk of boiling alcohol. As thus purified it consists of a mass of white, asbestos-like needles which rapidly become brownish-white, and if not dried rapidly lose iodine; when dry, there seems to be no tendency for this decomposition to take place. When heated, the substance does not melt, but is decomposed at about  $230^{\circ}$ , with much charring and liberation of iodine. The substance contains water of crystallisation, and the estimation of the amount of this presents some difficulty, as, if the substance is dried in the air, decomposition takes place, whilst if it is dried in a desiccator a certain amount of  $H_2O$  is lost. The following figures were obtained from a sample which had been dried as rapidly as possible in a desiccator over sulphuric acid.

0.1015 gave 0.0393  $BaSO_4$ .  $Ba = 22.7$ .

0.0789 „ 0.0607  $AgI$ .  $I = 41.7$ .

0.1976 lost 0.0096  $H_2O$ .  $H_2O = 4.8$ .

$Ba(OH)_2I_2 \cdot C_7H_8O_3 \cdot 2H_2O$  requires  $Ba = 22.6$ ;  $I = 42.2$ ;  $H_2O = 5.9$  percent.

0.1879 of anhydrous salt gave 0.0753  $BaSO_4$ .  $Ba = 23.6$ .

$Ba(OH)_2I_2 \cdot C_7H_8O_3$  requires  $Ba = 24.2$  per cent.

From the extreme ease with which this compound is broken up, yielding the substance  $C_7H_7O_3I$ , it is evident that only one half of the iodine present is associated with the barium in the molecule.

#### *Action of Iodine on the Sodium Salt of Dimethylpyrone.*

The sodium salt prepared from dimethylpyrone and also a sample prepared from diacetylacetone were suspended in 99.8 per cent. alcohol (if 98 per cent. alcohol is used, diacetylacetone is produced) and treated with iodine. Two atoms of iodine only were required for each molecule of salt containing 2 atoms of sodium. From both salts, the compound  $C_7H_7O_3I$  is produced, and from neither has it been found possible to isolate a sodium salt corresponding to the barium derivative just described.

The action of iodine on the compound  $C_7H_8O_2 \cdot NaOEt$  was also examined, but no satisfactory result was obtained.

RESEARCH LABORATORY OF THE

PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

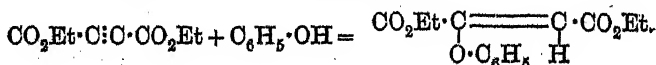
CII.—*Condensation of Phenols with Esters of the Acetylene Series. Part II. Action of Phenols on Ethyl Phenylpropiolate and Ethyl Acetylenedicarboxylate.*

By SIEGFRIED RUHEMANN and FRED BEDDOW, D.Sc., Ph.D.

FROM  $\beta$ -hydroxycinnamic acid, two stereoisomeric ethers can be derived, represented by the following formulæ in which R denotes a hydrocarbon group:



It has recently been shown (this vol., 984) that the aryl ethers of ethyl  $\beta$ -hydroxycinnamate are readily formed by the union of the sodium phenolates with ethyl phenylpropiolate, and that ethyl  $\beta$ -phenoxy-cinnamate and ethyl  $\beta$ -*p*-cresoxy-cinnamate slowly solidify on standing, to form colourless crystals which melt about 70°. These facts seem to point to the conclusion that the compounds of type I are first produced, but change under certain conditions into those of type II. The conditions which produce this change and the reasons why ethyl  $\beta$ -*o*-cresoxy-cinnamate, described in our previous paper, and ethyl  $\beta$ -*m*-cresoxy-cinnamate, described in this, show no signs of solidifying have still to be ascertained. That such a transformation does take place seems to be proved by a study of the compounds formed by the action of sodium phenolates on ethyl acetylenedicarboxylate. In this case, it would be expected that the union would lead to the aryl ethers of ethyl hydroxymaleate, thus



We find, however, that on proceeding in the same way as described for the preparation of the aryl ethers of ethyl  $\beta$ -hydroxycinnamate, the aryl ethers of ethyl hydroxyfumarate are formed instead of those of ethyl hydroxymaleate. This has been proved by a comparison of these esters and their acids with the compounds which we have obtained by the action of the sodium phenolates on ethyl chlorofumarate.

The aryl ethers of hydroxyfumaric acid differ from the corresponding ethers of  $\beta$ -hydroxycinnamic acid, inasmuch as the latter on heating lose carbon dioxide and yield phenoxystyrene and its homologues, whilst the former are transformed into the ethers of hydroxymaleic acid. The members of these two classes show characteristic differences; the aryl ethers of hydroxymaleic acid are distinguished from

the ethers of hydroxyfumaric acid by their crystalline form, their lower melting point, their greater solubility in water, and especially by the circumstance that they are colourless, whilst the isomerides are yellow. Moreover, on adding lead acetate to the aqueous solutions of the aryl ethers of hydroxymaleic acid, crystals of the corresponding lead salts separate, whilst the ethers of hydroxyfumaric acid do not yield precipitates under the same conditions. This behaviour is similar to that of lead acetate towards dibromomaleic and dibromofumaric acids (Bandrowski, *Ber.*, 1879, 12, 2214; Michael, *J. pr. Chem.*, 1892, [ii], 46, 7).

## EXPERIMENTAL.

*Ethyl β-m-Cresoxycinnamate*,  $C_6H_5 \cdot C(O \cdot C_6H_4 \cdot CH_3) \cdot CH \cdot CO_2C_2H_5$ .

For the preparation of this compound, we have used the same method as in the previous cases (*loc. cit.*). On adding 17.4 grams of ethyl phenylpropiolate to the hot magma obtained by dissolving 2.3 grams of sodium in excess of *m*-cresol, the solid disappears and a dark, viscous product results. This is well shaken with dilute sulphuric acid and ether, and the ethereal layer freed from the cresol by agitation with dilute caustic potash solution, washed with water, and dried with calcium chloride. After removal of the ether by evaporation, the remaining oil distils in a vacuum. The yield is almost quantitative. The ester boils at 217° under 12 mm. pressure and shows no signs of solidifying. On analysis:

0.2033 gave 0.5710  $CO_2$  and 0.1165  $H_2O$ .  $C = 76.60$ ;  $H = 6.36$ .

$C_{18}H_{18}O_3$  requires  $C = 76.59$ ;  $H = 6.38$  per cent.

*β-m-Cresoxycinnamic acid*,  $C_6H_5 \cdot C(O \cdot C_6H_4 \cdot CH_3) \cdot CH \cdot CO_2H$ , is obtained by hydrolysis of the ester with alcoholic potash; after the alkaline solution has been freed from alcohol as completely as possible, by heating on the water-bath, the liquid is diluted with water and acidified with sulphuric acid; the *β-m*-cresoxycinnamic acid separates as an oil which gradually solidifies. After recrystallisation from dilute alcohol, colourless leaflets are obtained which melt and decompose at 126°. On analysis:

0.2012 gave 0.5580  $CO_2$  and 0.1002  $H_2O$ .  $C = 75.63$ ;  $H = 5.53$ .

$C_{18}H_{14}O_3$  requires  $C = 75.59$ ;  $H = 5.51$  per cent.

The acid dissolves freely in ether, alcohol, or chloroform, but only sparingly in boiling water. Its solution in ammonia yields, with silver nitrate, a white precipitate of the silver salt; this is neither changed on exposure to light, nor decomposed on drying at 100°. On analysis:

0.2323 left, on ignition, 0.0695 Ag.  $Ag = 29.91$ .

$C_{16}H_{18}OAg_3$  requires  $Ag = 29.91$  per cent.



*m*-Cresoxystyrene,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3) : \text{CH}_2$ , is formed by heating the acid and distilling the oil which remains behind after carbon dioxide has ceased to be evolved. It is a colourless oil which boils at  $167\text{--}168^\circ$  under 12 mm. pressure and its density  $d_{23^\circ/23^\circ}$  is 1.0484. On analysis:

0.1953 gave 0.6120  $\text{CO}_2$  and 0.1162  $\text{H}_2\text{O}$ .  $\text{C} = 85.46$ ;  $\text{H} = 6.61$ .

$\text{C}_{15}\text{H}_{14}\text{O}$  requires  $\text{C} = 85.71$ ;  $\text{H} = 6.67$  per cent.

*m*-Cresoxystyrene, like its isomerides and phenoxystyrene, is decomposed by heating with dilute hydrochloric acid, and yields acetophenone and *m*-cresol.

#### *Action of Phenols on Ethyl Acetylenedicarboxylate.*

In preparing the ethyl acetylenedicarboxylate required for this work, it was found that when the esterification was effected by using sulphuric acid, as described by Michael (*J. pr. Chem.*, 1892, [ii], 46, 7), the yield was unsatisfactory, but that it becomes almost quantitative if an absolute alcoholic solution of acetylenedicarboxylic acid is saturated with hydrogen chloride, and after allowing the mixture to stand overnight, the product is poured on to ice, and the oil which separates is shaken with dilute sodium carbonate, dried with calcium chloride, and distilled under diminished pressure.

#### *Ethyl Phenoxyfumarate*, $\text{CO}_2\text{C}_2\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_5) : \text{CH} \cdot \text{CO}_2\text{C}_2\text{H}_5$ .

The union of sodium phenolate with ethyl acetylenedicarboxylate is effected in the same manner as with ethyl phenylpropiolate. The oil obtained after removal of the excess of phenol by shaking the product with caustic potash is fractionated in a vacuum. The larger portion boils at  $183\text{--}184^\circ$  under 14 mm. pressure, and is ethyl phenoxyfumarate; its density  $d_{26^\circ/26^\circ}$  is 1.1274. A smaller quantity of a yellowish oil is also formed; this distils over at  $220\text{--}230^\circ$  under the same pressure, and has not been further examined. Ethyl phenoxyfumarate was analysed, with the following results:

0.1953 gave 0.4549  $\text{CO}_2$  and 0.1053  $\text{H}_2\text{O}$ .  $\text{C} = 63.52$ ;  $\text{H} = 5.99$ .

$\text{C}_{14}\text{H}_{16}\text{O}_5$  requires  $\text{C} = 63.63$ ;  $\text{H} = 6.06$  per cent.

*Phenoxyfumaric acid*,  $\text{CO}_2\text{H} \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_5) : \text{CH} \cdot \text{CO}_2\text{H}$ .—On boiling the ester with alcoholic potash on the water-bath for 1 hour, hydrolysis takes place, and after evaporation of the alcohol, a solid is left behind which readily dissolves in water. From the alkaline solution, the acid is partially precipitated by dilute sulphuric acid, whilst the remainder is extracted with ether. The acid dissolves freely in alcohol or ether, and crystallises from boiling water in yellowish plates which retain their

colour, even after frequent recrystallisation and the use of animal charcoal. Phenoxyfumaric acid melts and decomposes at  $215^{\circ}$ , becoming dark a few degrees below this. On analysis:

0.2000 gave 0.4237  $\text{CO}_2$  and 0.0727  $\text{H}_2\text{O}$ .  $\text{C} = 57.74$ ;  $\text{H} = 4.03$ .

$\text{C}_{10}\text{H}_8\text{O}_5$  requires  $\text{C} = 57.69$ ;  $\text{H} = 3.84$  per cent.

On adding silver nitrate to a solution of the acid in ammonia, a white silver salt is precipitated; this can be dried at  $100^{\circ}$ , but decomposes suddenly on heating to a higher temperature. On analysis:

0.2630 left, on ignition, 0.1338 Ag.  $\text{Ag} = 50.87$ .

$\text{C}_{10}\text{H}_6\text{O}_5\text{Ag}_2$  requires  $\text{Ag} = 51.18$  per cent.

*Phenoxyfumaramide*,  $\text{CONH}_2 \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_5) : \text{CH} \cdot \text{CONH}_2$ , separates as a white solid on allowing ethyl phenoxyfumarate to remain in contact with strong aqueous ammonia for 2 days. It is sparingly soluble in alcohol, but dissolves in a large quantity of boiling water, and crystallises in small, colourless prisms which melt at  $235^{\circ}$  to a brown liquid. On analysis:

0.1965 gave 24 c.c. moist nitrogen at  $25^{\circ}$  and 760 mm.  $\text{N} = 13.61$ .

$\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2$  requires  $\text{N} = 13.59$  per cent.

*Phenoxyfemaleic acid*,  $\text{CO}_2\text{H} \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_5) : \text{CH} \cdot \text{CO}_2\text{H}$ .—If phenoxyfumaric acid is heated in a vacuum, it partially decomposes and evolves carbon dioxide, but a portion distils over at  $197^{\circ}$  under about 10 mm. pressure; the distillate is an oil which solidifies on cooling. This substance is undoubtedly the anhydride of phenoxyfemaleic acid; it dissolves in hot water, and the solution, on cooling, deposits colourless needles which melt at  $168^{\circ}$ , dissolve freely in alcohol or ether, and are slightly soluble in cold water. On analysis:

0.2007 gave 0.4220  $\text{CO}_2$  and 0.0700  $\text{H}_2\text{O}$ .  $\text{C} = 57.34$ ;  $\text{H} = 3.87$ .

0.1994 „ 0.4220  $\text{CO}_2$  „ 0.0723  $\text{H}_2\text{O}$ .  $\text{C} = 57.71$ ;  $\text{H} = 4.02$ .

$\text{C}_{10}\text{H}_8\text{O}_5$  requires  $\text{C} = 57.69$ ;  $\text{H} = 3.84$  per cent.

On titration: 0.2080 gram was neutralised by 20 c.c. of  $N/10$  sodium hydroxide, which is the calculated amount for a dibasic acid of the formula  $\text{C}_{10}\text{H}_8\text{O}_5$ . In this and the subsequent titrations, the imide of dicinnamylphenylazimide, obtained by one of us (Trans., 1892, 61, 278), was used as indicator instead of litmus, which proved to be unsatisfactory.

Phenoxyfemaleic acid, as previously mentioned (p. 1120), is distinguished from its stereoisomeride, not only by its melting point and the colour, but also by its behaviour towards lead acetate, since in aqueous solution it gives with the acetate colourless needles of the lead

The *silver* salt was obtained by adding silver nitrate to the solution of the acid in ammonia ; it explodes on heating.

*Action of Sodium Phenolate on Ethyl Chlorofumarate.*

Although the behaviour of the ester, which is formed by the union of sodium phenolate with ethyl acetylenedicarboxylate, characterises it as ethyl phenoxyfumarate, yet we have thought it advisable to supply further evidence by a comparison of this ester with the product of the action of the phenolate on ethyl chlorofumarate.

In order to effect this reaction, it is best to use the method which served for the formation of ethyl phenoxyfumarate from ethyl acetylenedicarboxylate, that is, by adding ethyl chlorofumarate to the hot solution of sodium in an excess of phenol, and isolating the ester in the manner previously described. Its identity with the compound formed from acetylenedicarboxylic acid was ascertained from the boiling point and the following analysis :

0.1912 gave 0.4449  $\text{CO}_2$  and 0.1058  $\text{H}_2\text{O}$ .  $\text{C} = 63.46$  ;  $\text{H} = 6.14$ .

$\text{C}_{14}\text{H}_{16}\text{O}_5$  requires  $\text{C} = 63.63$  ;  $\text{H} = 6.06$  per cent.

The properties of the acid which is formed on hydrolysis of this ester agree in every respect with those stated above for phenoxyfumaric acid. Its composition was, moreover, verified by the following titration :

0.2077 gram was neutralised by 20 c.c. of *N*/10 sodium hydroxide, instead of 19.975 c.c. as required for a dibasic acid of the formula  $\text{C}_{10}\text{H}_8\text{O}_5$ .

We have also distilled this acid in a vacuum and found that the distillate, on recrystallisation from water, yields phenoxy-maleic acid, identical with the specimen which we obtained from the product of the union of sodium phenolate with ethyl acetylenedicarboxylate.

These experiments prove that the esters which are formed by the interaction of sodium phenolate with ethyl acetylenedicarboxylate on the one hand and ethyl chlorofumarate on the other, yield the same acid, namely, phenoxyfumaric acid, on hydrolysis. This fact leads to the conclusion that the esters also are identical. This view is supported by the identity of the boiling points, and the fact that on hydrolysis of the ester a transformation of the maleoid into the fumaroid form does not take place, since phenoxy-maleic acid on heating with alcoholic potash on the water-bath remains unchanged.

*Ethyl o-Cresoxyfumarate*,  $\text{CO}_2\text{C}_2\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3)\cdot\text{CH}\cdot\text{CO}_2\text{C}_2\text{H}_5$ .

Sodium *o*-cresolate reacts with ethyl acetylenedicarboxylate, forming an ester which is isolated in the same manner as in the previous cases. It is a colourless oil which boils at  $184\text{--}185^\circ$  under 14 mm. pressure; its density  $d_{26^\circ/26^\circ}$  is 1.1137. On analysis:

0.1980 gave 0.4681  $\text{CO}_2$  and 0.1170  $\text{H}_2\text{O}$ . C = 64.47; H = 6.56.

$\text{C}_{15}\text{H}_{18}\text{O}_5$  requires C = 64.74; H = 6.47 per cent.

On hydrolysis of the ester with alcoholic potash, the acid  $\text{CO}_2\text{H}\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3)\cdot\text{CH}\cdot\text{CO}_2\text{H}$  is formed; this is readily soluble in ether or alcohol, and sparingly so in boiling water. From the last solvent, the acid crystallises out as yellow spherules which melt at  $222^\circ$  with an evolution of gas. On analysis:

0.1986 gave 0.4332  $\text{CO}_2$  and 0.0790  $\text{H}_2\text{O}$ . C = 59.48; H = 4.41.

$\text{C}_{11}\text{H}_{10}\text{O}_5$  requires C = 59.46; H = 4.50 per cent.

Both compounds, the ester and the acid, belong to the fumaroid series, being therefore ethyl *o*-cresoxyfumarate and *o*-cresoxyfumaric acid, since the same substances are formed on using ethyl acetylenedicarboxylate and ethyl chlorofumarate (as shown by the identity of their boiling points and densities).

The composition of the ester obtained by the interaction of sodium cresolate and ethyl chlorofumarate was verified by the following analysis:

0.1987 gave 0.4698  $\text{CO}_2$  and 0.1190  $\text{H}_2\text{O}$ . C = 64.48; H = 6.65.

$\text{C}_{15}\text{H}_{18}\text{O}_5$  requires C = 64.74; H = 6.47 per cent.

The acid derived from this ester gave on titration the following results: 0.2056 gram was neutralised by 18.5 c.c. of *N*/10 sodium hydroxide, instead of by 18.52 c.c. as required for a dibasic acid of the formula  $\text{C}_{11}\text{H}_{10}\text{O}_5$ .

*Ethyl m-Cresoxyfumarate*,  $\text{CO}_2\text{C}_2\text{H}_5\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3)\cdot\text{CH}\cdot\text{CO}_2\text{C}_2\text{H}_5$ .

Since it was found that the same products are formed, whether sodium phenolates react with ethyl acetylenedicarboxylate or with ethyl chlorofumarate, the latter has been employed for the preparation of ethyl *m*-cresoxyfumarate. The ester distils at  $192^\circ$  under a pressure of 14 mm., and its density  $d_{26^\circ/26^\circ}$  is 1.1115. On analysis:

0.1850 gave 0.4374  $\text{CO}_2$  and 0.1090  $\text{H}_2\text{O}$ . C = 64.48; H = 6.54.

$\text{C}_{15}\text{H}_{18}\text{O}_5$  requires C = 64.74; H = 6.47 per cent.

*m*-Cresoxyfumaric acid is obtained by hydrolysis of the ester with

alcoholic potash; it readily dissolves in alcohol and ether, but only sparingly in water. After recrystallisation from a hot aqueous solution, it is obtained in the form of yellowish groups of needles which melt at  $240^{\circ}$  with an evolution of gas. On analysis:

0.1905 gave 0.4135  $\text{CO}_2$  and 0.0778  $\text{H}_2\text{O}$ .  $\text{C} = 59.20$ ;  $\text{H} = 4.53$ .

$\text{C}_{11}\text{H}_{10}\text{O}_5$  requires  $\text{C} = 59.46$ ;  $\text{H} = 4.50$  per cent.

0.1187 gram was neutralised by 10.7 c.c. of  $N/10$  sodium hydroxide, the amount calculated for the substance  $\text{C}_{11}\text{H}_{10}\text{O}_5$  being 10.69 c.c.

*m-Cresoxymaleic Acid*.—On heating *m*-cresoxyfumaric acid in a vacuum, it partially decomposes and yields a distillate which crystallises from boiling water in colourless needles melting (not sharply) at  $208^{\circ}$ . On titration:

0.0765 gram was neutralised by 7 c.c. of  $N/10$  sodium hydroxide, instead of 6.89 c.c. as required for a dibasic acid of the formula  $\text{C}_{11}\text{H}_{10}\text{O}_5$ .

Lead acetate gives with a hot aqueous solution of *m*-cresoxymaleic acid a lead salt which gradually separates in groups of needles. On the other hand, no precipitate is formed with *m*-cresoxyfumaric acid. These stereoisomeric acids therefore resemble phenoxymaleic and phenoxyfumaric acids respectively in their behaviour towards lead acetate.

*Ethyl p-Cresoxyfumarate*,  $\text{CO}_2\text{C}_2\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3) : \text{CH} \cdot \text{CO}_2\text{C}_2\text{H}_5$ .

Sodium *p*-cresolate yields with ethyl chlorofumarate the ethyl ester of *p*-cresoxyfumaric acid, which is isolated from the product of the reaction in the usual way. It distils at  $191$ – $192^{\circ}$  under 12 mm. pressure, and its density  $d_{26^{\circ}/26^{\circ}}$  is 1.1132. On analysis:

0.1981 gave 0.4698  $\text{CO}_2$  and 0.1186  $\text{H}_2\text{O}$ .  $\text{C} = 64.67$ ;  $\text{H} = 6.65$ .

$\text{C}_{15}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 64.74$ ;  $\text{H} = 6.47$  per cent.

In conclusion, it may be mentioned that the research on the additive compounds of the esters of the acetylene series on the lines indicated in this paper is still being pursued.

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### CIII.—*Vapour Pressures, Specific Volumes, and Critical Constants of Diisopropyl and Diisobutyl.*

By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

A COMPARISON of the constants for normal and isopentane (Trans., 1897, 71, 446; *Proc. Phys. Soc.*, 1895, 13, 602) on the one hand, and for methyl butyrate and isobutyrate (Trans., 1893, 63, 1191) on the other, seemed to show that the deviations from the generalisations of van der Waals in the case of isomeric substances are intimately connected with their constitution.

In order to obtain further light on this point, it was decided to prepare specimens of diisopropyl and diisobutyl, so as to compare them with the corresponding normal paraffins.

#### *Preparation of the Paraffins.*

Specimens of these substances were first prepared by the action of sodium on isopropyl iodide and isobutyl bromide respectively in ethereal solution. No great difficulty was experienced in the preparation of diisobutyl, and the yield was fair. As the boiling point of the paraffin ( $109.2^{\circ}$ ) is considerably higher than that of isobutyl bromide ( $92.3^{\circ}$ ), it could be separated fairly completely from the unaltered bromide by fractional distillation. The final purification was effected by treatment with a mixture of nitric and sulphuric acids, and subsequent fractional distillation through a twelve-column Young and Thomas dephlegmator. Owing to the partial conversion of isobutyl bromide into the tertiary bromide, a small quantity of hexamethylethane is formed, but this is completely removed during the fractional distillation.

It is impossible to prepare a pure specimen of diisopropyl from isopropyl bromide, as the boiling points are almost the same, and on treatment of the mixture with nitric and sulphuric acids, bromine is set free, and at once acts on the paraffin.

Even from isopropyl iodide, the preparation is difficult and the yield very poor. Thus Zander (*Annalen*, 1882, 214, 167) obtained only 5 per cent. of the theoretical yield of diisopropyl as against 24 per cent. of normal hexane from propyl iodide.

As has been pointed out by Silva (*Ber.*, 1872, 5, 984), sodium has no action on a dry ethereal solution of isopropyl iodide, and a little water has therefore to be added. In this case, however, propyl iodide is evolved in large quantity, and naturally carries away a good deal

of the volatile hydrocarbon. We were, however, successful in obtaining a sufficient quantity of the paraffin by this method. The ether and iodide were removed for the most part by a preliminary fractionation; the rest of the ether was then dissolved out by strong sulphuric acid, and the diisopropyl finally completely freed from the iodide, which boils more than  $30^{\circ}$  higher, by fractional distillation through a five-column "evaporator" still-head. Several determinations of the specific gravity at  $0^{\circ}$  were made during the final stages of the fractionation, and the agreement between them, as well as the constancy of the boiling point, afforded a strong presumption in favour of the purity of the substance. Another small specimen, similarly prepared, had the same specific gravity.

It is, however, remarkable that whilst the specific gravities of the isoparaffins are, so far as is known, invariably lower than those of the corresponding normal hydrocarbons, and whilst diisobutyl is considerably lighter than normal octane, our specimen of diisopropyl was found to be actually heavier than normal hexane. At the same time, it may be pointed out that the specific gravities of diisopropyl obtained by other observers are, with one very doubtful exception, higher than ours (p. 1132).

To obtain further confirmation of the correctness of our result, it seemed desirable, if possible, to prepare a second specimen by an entirely different method.

Diisopropyl is stated to have been prepared by a number of reactions, which might be expected to yield normal hexane, but the products obtained, judging from the range of boiling point given, appear to have been very impure. Of the methods which do not involve a radical change in the constitution, the electrolysis of potassium isobutyrate seemed the most promising. In order to test the method, a preliminary preparation of diisobutyl from potassium isovalerate was made, because it seemed probable that the yield would be better, whilst the loss by evaporation would naturally be far less. As there was no doubt about the purity of our specimen of diisobutyl, it was not thought necessary to spend time over the purification of the isovaleric acid by fractional distillation, and, as a consequence, the product obtained was mixed with small quantities of its homologues or isomerides. The object of the investigation was, however, attained, inasmuch as we were able to ascertain the right conditions for a satisfactory yield of hydrocarbon. It may be mentioned that, with the apparatus used, and with a strong and slightly acid solution of the potassium salt, the yield of hydrocarbon was large compared with that of isobutyl isovalerate, or of isobutylene.

The electrolytic cell was similar in principle to that employed by Professor Kuenen, to whom, as well as to Professor Walker, we

are indebted for valuable suggestions. The anode consisted of four rings of platinum wire about 4 cm in diameter, welded to three long, vertical platinum wires which passed above into a J-shaped manometer tube containing mercury, which served for making contact.

The anode was placed in a vessel constructed in the following manner. A wide-mouthed bottle was cut off a little below the neck, and for the bottom part of the bottle was substituted a porous pot of the same diameter, the surfaces of contact being carefully ground and the two portions attached by an indiarubber connection. The mouth of this vessel was provided with an indiarubber stopper perforated with two holes, through one of which passed the J-shaped tube, and through the other a vertical exit tube for gases. The cathode, of stout amalgamated zinc, and the porous pot which it nearly surrounded, were placed in a wide, cylindrical, glass vessel, which during the experiment was cooled by ice. The current used was about 6.5 amperes, and the voltage nearly 10.

A 30 to 35 per cent. solution of caustic potash was neutralised with *isovaleric* acid, and a little more acid added. The porous pot and outer vessel were filled with the solution, and the current was passed for about 3 hours in each operation. The amount of *isobutylene* was roughly estimated by absorption in bromine, after removal of the carbon dioxide.

The oil from the porous cell was separated and distilled through a "pear" still-head with twelve bulbs, and was found to consist of *diisobutyl isobutyl isovalerate*, and free *isovaleric* acid. The portion boiling from about 108° to 120° amounted, on an average, to about 7.5 grams in each operation. The total quantity, 45.2 grams, resulting from about 18 hours' electrolysis, was treated with potash to remove free acid, boiled with strong potash to hydrolyse any ester, washed with water, shaken twice with strong sulphuric acid, and finally washed with water, dried with phosphoric oxide, and distilled through a five-column "evaporator" still-head. Very nearly 10 grams were collected between 109.15° and 109.2° (corr. to 760 mm.), and a second 10 grams from 109.2° to 109.25°. The specific gravities at 0° were 0.71066 and 0.71092 respectively, that of the pure specimen obtained from *isobutyl* bromide being 0.71021. Considering that the quantity of *diisobutyl* prepared was insufficient for complete purification by fractional distillation, the agreement may be regarded as satisfactory. The amount of *isobutyl isovalerate* was estimated by neutralising the distillate from 120° to 176°, so as to remove free acid.



Kahlbaum, was carefully fractionated with a "pear" still-head, 780 grams of the acid, boiling within  $0.05^{\circ}$ , being obtained. The strength of the solution, the current, and the electrolytic cell were the same as in the case of potassium *isovalerate*, but owing to the fact that the quantity of *diisopropyl* formed was so small as to be almost entirely carried forward by the gases evolved in the porous pot, it was found necessary to devise a method for absorbing the carbon dioxide and propylene without injuring or losing the *diisopropyl*. The absorbents finally used were a strong solution of caustic potash and strong sulphuric acid. The former was contained in a nearly horizontal absorption tube provided with safety bulbs at either end, and a short, narrow tube with a stop-cock for running off the liquid and separating any oil at the end of the experiment. The acid was contained in a sloping tube with eighteen small bulbs; this was similarly provided with large safety bulbs and stoppered exit tube. The absorption of both carbon dioxide and propylene was practically complete.

During each operation, it was found that a very small quantity of oil collected on the surface of the potash, and a relatively much larger quantity over the sulphuric acid. These were accumulated in separate small flasks, to be worked up when the quantity was sufficient.†

The liquid from the porous pot was not placed in a separating funnel on account of the volatility of the paraffin, but was distilled each time until the temperature reached about  $98^{\circ}$ , the distillate being collected in a tube cooled by a freezing mixture.\* This was found convenient, for the water that came over froze, and the oil could be poured from the ice with scarcely any loss.

The sulphuric acid from the absorption tube, in the first two or three cases, was diluted and distilled in a similar manner, but the quantity of *diisopropyl* was inappreciable, the distillate consisting of *isopropyl* alcohol, together with polymerides of propylene in small quantity, most of the latter, however, remaining behind in the distilling flask. After obtaining a sufficient quantity of *isopropyl* alcohol to identify it, the treatment of the sulphuric acid was discontinued. There were thus, at the end of the operations, three quantities of oil to work up: A, that from the porous pot; B, that from the potash tube; C, that from the sulphuric acid bulbs.

A. The liquid was distilled through the five-column "evaporator" still-head until the temperature rose to  $80^{\circ}$ , in order to separate any *diisopropyl*. The residue, kept cool by running water, was mixed with strong sulphuric acid, in which it dissolved completely. After standing for some time, it was diluted, and the oil that separated was

\* In order to avoid loss of *diisopropyl* by evaporation during the various processes involved in its isolation, the receivers were in all cases cooled by freezing mixtures.

removed, treated with caustic soda, washed with water, and, lastly, dried and freed from any remaining isopropyl alcohol by the repeated addition of small quantities of phosphoric oxide until the latter remained in a floury condition. It was then distilled from phosphoric oxide and fractionated with a "pear" still-head. The weight of isopropyl isobutyrate, boiling from about  $117^{\circ}$  to  $125^{\circ}$ , was 38 grams, and from this 21 grams of ester, boiling constantly at  $120\text{--}75^{\circ}$ , was obtained.

B. The distillate from A boiling below  $80^{\circ}$  was mixed with B. It was found to be almost completely soluble in strong sulphuric acid, and the small remaining layer boiled between  $56^{\circ}$  and  $70^{\circ}$ , mostly at  $58^{\circ}$ , and consisted, therefore, mainly of diisopropyl. The ester, which separated on dilution of the sulphuric acid solution, was found to be practically free from diisopropyl.

C. This oil was first distilled with steam; the quantity that came over below about  $90^{\circ}$  was disappointingly small, a considerable amount of heavy oil, consisting, doubtless, of polymerides of propylene, remaining in the flask. The distillate, separated from the water and dried, was redistilled, and the portion boiling within about the same limits of temperature was collected with the diisopropyl from B. The total weight was only 3.4 grams. A relatively large amount of diisopropyl was lost in the preliminary experiments, but, even under the best conditions, 100 grams of isobutyric acid gave only 1.5 grams of moderately pure diisopropyl, the theoretical yield being 49 grams.\*

The crude paraffin was dried with a little phosphoric oxide and redistilled, when it boiled from  $57.6^{\circ}$  to  $62.5^{\circ}$ , the greater part coming over at about  $58^{\circ}$ . The weight was now 2.6 grams, and the specific gravity at  $0^{\circ}$  was found to be 0.6811, as against 0.6797 for the specimen prepared from isopropyl iodide, when determined in the same small apparatus.

The diisopropyl was redistilled three times from a little phosphoric oxide, the temperature not rising higher the last time than  $58.8^{\circ}$ , and remaining fairly constant at about  $58.0^{\circ}$  during the greater part of the distillation. The specific gravity at  $0^{\circ}$  had now fallen to 0.6806, and it is evident that further redistillation would not have lowered it below that found for the other specimen. Inasmuch as polymerides of propylene were formed in presence of the strong sulphuric acid, it was still possible that a hexylene, boiling at about the same temperature as diisopropyl, might be present. It was found, however, that the

\* Dr. J. Petersen, of Copenhagen, states (*Bull. Acad. roy. Danemark*, 1897, 397; *Zeit. physikal. Chem.*, 1900, 33, 99) that the yield of diisopropyl obtained by the electrolysis of potassium isobutyrate is exceedingly small compared with that of isopropyl isobutyrate from the same salt, or of normal hexane from potassium butyrate.

small residues from the later distillations referred to had practically no decolorising action on bromine.

The main object of the investigation was therefore attained, since it was proved that the specific gravity of pure diisopropyl is not really lower than that obtained for the specimen from isopropyl iodide.

# THERMAL CONSTANTS OF DIISOPROPYL.

These constants were determined with the specimen from isopropyl iodide, that from potassium isobutyrate being too small and not sufficiently pure.

## Boiling Point.

Both hydrocarbons were distilled from phosphoric oxide immediately before being used for the determinations of specific gravity, vapour pressures, &c. There are, therefore, several observations of the boiling point of each substance.

Pressure.	Temperature.	
	Observed.	Corrected to 760 mm.
755.6	57.85°	58.05°
753.9	57.80	58.05
752.3	57.75	58.05
753.3	57.9	58.15

Mean 58.08

Calculated from the constants for Biot's formula, the boiling point is 58.10°, and the value of  $dp/dt$  at the boiling point is 24.26 mm. per degree.

## Boiling points given by other observers.

Name.	Reference.	Boiling point.
Schorlemmer...	<i>Annalen</i> , 1867, 144, 184.	58°
Zander .....	<i>Annalen</i> , 1882, 214, 167.	58
Engler .....	<i>Ber.</i> , 1889, 22, 595.	57—59
Riche .....	<i>Ann. Chim. Phys.</i> , 1860, [iii], 59, 426.	56—58
Aschan .....	<i>Ber.</i> , 1898, 31, 1801.	57—59

Schorlemmer's and Zander's specimens were prepared from isopropyl iodide and sodium; Engler's from whale oil by destructive distillation; Riche's by heating cenanthylic acid with barium oxide, whilst Aschan's was separated from Baku petroleum.

*Specific Gravity.*

The specific gravities of two different specimens were determined at  $0^{\circ}/4^{\circ}$  in a Sprengel tube as modified by Perkin; the weighings were reduced to a vacuum.

A.....	0.67951
B.....	0.67945
Mean	0.67948

*Specific gravities by other observers.*

	At $t^{\circ}$ .	Specific gravity.
		Reduced to $0^{\circ}/4^{\circ}$ .
Schorlemmer .....	0.6769 at $10^{\circ}$	0.6857
	0.6701 „ $17.5$	0.6858
	0.6569 „ $29.0$	0.6831
Zander.....	0.6680 „ $17.5$	0.6829
Engler.....	0.6677 „ $21$	0.6867
Riche .....		0.668
Aschan .....	0.66485 „ $17.25$	0.68173

There is some uncertainty about the reductions to  $0^{\circ}$ , as it is usually not stated whether the specific gravity is referred to water at  $4^{\circ}$ , at  $0^{\circ}$ , or at the same temperature ( $t$ ) as that of the substance. We have assumed that the water was at  $4^{\circ}$  in each case. If it had been at  $t^{\circ}$ , the reduced specific gravities would be slightly lower; thus Engler's would be 0.6853 instead of 0.6867.

The determination by Riche differs entirely from all the others, but many of the results described in his paper, such as the existence of a hexane boiling at  $78^{\circ}$ , are difficult to explain, and it seems most improbable that diisopropyl could be obtained from cenanthylic acid as he describes. Of the other results, those of Aschan and Zander agree best with ours, both being a little higher.

*Vapour Pressures at Low Temperatures.*

For pressures up to 320 mm., the method of Ramsay and Young was employed; from 240 mm. to the atmospheric pressure, a modified distillation bulb provided with a reflux condenser was used.

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
36.8 mm.	-13.5°	64.45 mm.	-3.4°	138.5 mm.	12.6°	238.7 mm.	25.55°
39.4	-12.45	77.9	+0.4	167.2	17.1	259.0	27.75
41.6	-11.45	92.25	3.85	200.2	21.25	278.5	29.5
51.65	-7.4	112.2	8.25	219.8	23.6	299.5	31.4
242.65	25.65	324.9	33.25	444.2	41.9	591.4	50.4
275	27.70	362.3	36.25	488.8	44.65	646.6	53.3
	30.35	403.2	39.2	533.7	47.55	694.3	55.85

The vapour pressures at high temperatures were determined with the pressure apparatus employed in previous researches. The observed pressures (the mean of four readings in each case), together with those read from the curves constructed from the observations at low temperatures, and also the pressures calculated by means of Biot's formula,

$$\log p = a + ba^t + c\beta^t,$$

are given in the following table.

The constants for Biot's formula are :

$$\begin{aligned} a &= 14.002278 \\ b &= -10.645849 & \log. b &= 1.0271804 \\ c &= -1.699429 & \log. c &= 0.2303031 \\ \log. a &= 1.99979200 \\ \log. \beta &= 1.99533068 \\ t &= t^\circ C + 10. \end{aligned}$$

### Vapour pressures.

Tem- perature.	Dynamical method from curve.	Statical method.	Calculated from Biot's formula.	Tem- perature.	Statical method.	Calculated from Biot's formula.
-10°	45.20 mm.		45.4 mm.	140°	5717 mm.	5697 mm.
0	75.95		76.05	150	6884	6879
10	128.45		122.25	160	8256	8234
20	190.55		189.4	170	9806	9781
30	285.1		288.8	180	11535	11536
40	411.6		412.6	190	13475	13519
50	584.8		584.1	200	15693	15752
60		807 mm.	806.8	210	18208	18258
70		1098	1090.3	216	19848	—
80		1444	1444.8	220	21009	21062
90		1876	1880.9			
100		2411	2409.7	225	22588	—
110		3044	3043.0			
120		3790	3798.2	227.35	23860	23880
130		4677	4673	(critical)		

The critical temperature was taken to be 227.40°, and the critical pressure 23,345 mm.

*Volumes of a Gram of Liquid.*

These were determined in the pressure apparatus; up to 150°, the volumes were read directly, but at higher temperatures they were calculated from observations of the volume of vapour and the total volume of liquid and vapour by the method previously described by one of us (Trans., 1893, 63, 1200).

The observed and smoothed specific volumes and the molecular volumes calculated from the smoothed specific volumes are given in the following table. The molecular weight is taken as 85·82.

*Volumes of a gram and molecular volumes of liquid.*

Temp.	Volumes of a gram in c.c.		Molecular volumes in c.c.	Temp.	Volumes of a gram in c.c.		Molecular volumes in c.c.
	Observed.	From curve.			Observed.	From curve.	
0°	1·4717	1·4717	126·30	140°	1·8744	1·8748	160·89
10	—	1·4909	127·95	150	1·9236	1·9240	165·12
20	—	1·5113	129·70	160	1·9813	1·9805	169·95
30	1·5327	1·5326	131·53	170	2·0482	2·0470	175·70
40	1·5551	1·5547	133·43	180	2·1260	2·1255	182·40
50	1·5775	1·5777	135·40	190	2·2149	2·2135	190·40
60	1·6018	1·6019	137·48	200	2·3394	2·3395	200·80
70	1·6270	1·6276	139·68	210	2·5070	2·5075	215·20
80	1·6568	1·6559	142·11	216	2·6610	2·6610	223·35
90	1·6866	1·6860	144·69	220	2·8048	2·8050	240·70
100	1·7182	1·7180	147·44	228	2·9660	2·9660	254·55
110	1·7517	1·7520	150·36	225	3·1263	3·1265	268·30
120	1·7889	1·7891	153·54	225·5	3·3699	3·3700	289·20
130	1·8307	1·8300	157·05	227·4 (critical)	—	4·148*	356·0*

\* By the method of Cailletet and Mathias corrected for the slight curvature of the "diameter."

*Volumes of a Gram of Saturated Vapour.*

Determinations were made with the pressure apparatus and by the sealed tube method (Trans., 1891, 59, 37; *Proc. Phys. Soc.*, 1895, 13, 617).

The results are given in the table below, also the volumes of a gram read from curves constructed by plotting the logarithms of the volumes against the temperatures. The molecular volumes calculated from the smoothed specific volumes are also given.

*Volumes of a gram and molecular volumes of saturated vapour.*

Temperature.	Volumes of a gram in c.c.				Molecular volumes in c.c.
	Pressure apparatus.	Sealed tube method.		From curves.	
		I.	II.		
50			379	392	33600
60			294	290	24900
70			219	219	18780
80			166	166.5	14290
90			129.0	129.0	11070
100			101.0	101.0	8670
110		75.2	80.1	80.0	6865
120		63.0	64.3	64.3	5515
130		51.4	51.9	52.0	4465
140		40.5		42.4	3635
150		34.3		35.4	3040
160	28.4	23.0		28.4	2440
170	23.25	23.35		23.30	2000
180	19.12	19.16		19.17	1645
190	15.76	15.64		15.72	1349
200	12.76	12.72		12.77	1095
210	10.15	10.13		10.14	870
216	8.61	8.64		8.60	738
220	7.575	7.57		7.57	650
223	6.710	6.74		6.72	577
225	6.065	—		6.065	520
226.5	5.400	—		5.410	464
227.4 (critical.)				4.148*	356.0*

\* By the method of Cailletet and Mathias corrected for the slight curvature of the "diameter."

The critical volume of a gram and the molecular volume were calculated from the critical density which was ascertained by the method of Cailletet and Mathias, taking into account the fact that the "diameter" is very slightly curved.

The densities of liquid and saturated vapour, the mean densities and those calculated from the formula

$$D_t = 0.3401 - 0.0004445t + 0.0000000413t^2$$

are given below.

The densities of saturated vapour below 50° were calculated from the vapour pressures on the assumption that the vapour densities are normal. The density at the critical point, calculated from the above formula, is 0.2411; from the simpler formula,

$$D_t = 0.3395 - 0.000433t,$$

it would be 0.2410. The difference is thus exceedingly small at the critical point, but would be much more marked at the lowest temperatures.

Temperature.	Densities.		Mean densities.		
	Liquid.	Saturated vapour.	Observed.	Calculated.	$\Delta \times 10^4$
0°	0.6795	0.0004	0.3399	0.3401	+2
10	0.6707	0.0006	0.3357	0.3357	0
20	0.6617	0.0009	0.3313	0.3312	-1
30	0.6525	0.0013	0.3269	0.3268	-1
40	0.6432	0.0018	0.3225	0.3224	-1
50	0.6338	0.0026	0.3182	0.3180	-2
60	0.6243	0.0034	0.3138	0.3136	-2
70	0.6144	0.0046	0.3095	0.3092	-3
80	0.6039	0.0060	0.3050	0.3048	-2
90	0.5931	0.0077	0.3004	0.3004	0
100	0.5821	0.0099	0.2960	0.2960	0
110	0.5708	0.0125	0.2916	0.2917	+1
120	0.5589	0.0156	0.2873	0.2874	+1
130	0.5464	0.0192	0.2828	0.2830	+2
140	0.5334	0.0236	0.2785	0.2787	+2
150	0.5197	0.0282	0.2740	0.2743	+3
160	0.5049	0.0352	0.2701	0.2701	0
170	0.4885	0.0429	0.2657	0.2657	0
180	0.4705	0.0522	0.2614	0.2614	0
190	0.4503	0.0636	0.2572	0.2571	-1
200	0.4274	0.0784	0.2529	0.2529	0
210	0.3988	0.0986	0.2487	0.2486	-1
216	0.3753	0.1163	0.2460	0.2460	0
220	0.3565	0.1321	0.2443	0.2443	0
223	0.3372	0.1488	0.2430	0.2431	+1
225	0.3198	0.1650	0.2424	0.2422	-2
226.5	0.2967	0.1849	0.2408	0.2415	+7
227.4	—	—	—	0.2441	

#### THERMAL CONSTANTS OF DIISOBUTYL.

The constants were determined with the specimen prepared by the action of sodium on isobutyl bromide.

#### Boiling point.

Pressure.	Temperature.	
	Observed.	Corrected to 760 mm.
748.65	108.65°	109.2°
752.3	108.85	109.2
746.5	108.6	109.25

Mean 109.2

From Biot's formula, b. p. = 109.2°;  $dp/dt = 20.9$  mm. per degree



*Boiling points given by other observers :*

Name.	Reference.	Observed.	Boiling Point.
			Corrected to 760 mm.
Kolbe.....	<i>Annalen</i> , 1849, 69, 259		108°
Kopp .....	<i>Annalen</i> , 1855, 95, 335	108·5° at 747·5	109·1
Thorpe ...	<i>Trans.</i> , 1880, 37, 219	108·2—108·7° at 748·2	108·53
Schiff .....	<i>Annalen</i> , 1883, 220, 88	107·8—107·9° at 751·4	108·25
Williams ..	<i>Annalen</i> , 1879, 35, 125	108·2° at 745	108·9
Pawlewski	<i>Ber.</i> , 1883, 16, 2634		107·5

Kolbe's specimen was obtained by the electrolysis of potassium *iso*-valerate. Most, if not all, of the others were prepared by the action of sodium on *isobutyl* bromide or iodide. Kopp's result agrees best with ours.

*Specific gravity.*

Temperature.	Specific gravity.
0°/4°	0·71021
11·9°/4°	0·69996

*Specific gravities determined by other observers.*

Name.	Reference.	Specific gravity	
		at <i>t</i> °.	Calculated at 0°/4°.
Kolbe .....	<i>Jahresb.</i> , 1848, 1, 559	0·6940 at 18°	0·7091
Wurtz .....	<i>Jahresb.</i> , 1855, 8, 576		0·7057
Kopp .....	<i>loc. cit.</i>		0·7135
Williams .....	<i>loc. cit.</i>		{ 0·7091 0·7085
Schorlemmer...	<i>Jahresb.</i> , 1867, 20, 567	0·698 at 16·5°	0·7119
Thorpe .....	<i>loc. cit.</i>		0·7111
Schiff .....	<i>loc. cit.</i>	0·7001 at 12·1°/4°	0·7103

Most of the above results are in fair agreement with ours, that of Schiff differing only slightly.

*Vapour pressures at low temperatures.*

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
8·70 mm.	3·55°	16·65 mm.	14·35°	38·15 mm.	29·85°	84·8 mm.	47·3°
9·50	4·75	19·8	16·7	45·35	33·45	96·2	50·8
10·70	6·75	22·4	19·65	53·35	37·15	108·8	53·3
12·00	8·6	28·4	24·2	61·35	40·05	122·5	56·15
13·9	11·2	32·35	26·55	72·5	43·6	138·45	59·1
158·25	62·05	248·0	73·95	373·2	86·0	552·2	98·25
177·55	65·05	278·3	77·25	410·8	88·9	603·2	101·3
197·6	67·35	307·0	80·05	455·3	92·15	657·0	104·25
221·8	70·9	339·6	83·05	501·5	95·2	715·2	107·2

*Constants for Biot's formula.*

$$\begin{aligned}
 a &= 2.918091 \\
 b &= 0.846986 & \log. b &= \bar{1}.9278763 \\
 c &= -2.628903 & \log. c &= 0.4197746 \\
 \log. a &= 0.00104426 \\
 \log. \beta &= \bar{1}.99619775 \\
 t &= t^{\circ}\text{C} - 10
 \end{aligned}$$

*Vapour pressures.*

Temperature	Dynamical method from curve.	Statistical method.	Calculated from Biot's formula.	Temperature.	Statistical method.	Calculated from Biot's formula.
0°	—		7.11	150°	2116	2118.2
10	13.0		13.0	160	2645	2630.6
20	23.05		22.77	170	3243	3231.3
30	38.5		38.19	180	3938	3930.2
40	61.8		61.68	190	4740	4738.0
50	95.95		96.19	200	5670	5666.5
60	145.2		145.35	210	6733	6729.5
70	213.3		213.3	220	7937	7941
80	305.5		304.9	230	9312	9319
90	426.6		425.6	240	10905	10833
100	578.8		581.15	250	12668	12654
110	777.1		777.9	260	14651	14660
120		1020	1022.6	270	16905	16929
130		1319	1322.5	276.8	18660	18640
140		1685	1684.9	(critical)		

*Volumes of a gram and molecular volumes of liquid.*

Temp.	Volumes of a gram in c.c.		* Molecular volumes in c.c.	Temp.	Volumes of a gram in c.c.		* Molecular volumes in c.c.
	Observed.	From curve.			Observed.	From curve.	
0°	1.4080	1.4080	160.17	150°	1.7483	1.7447	198.48
10	—	1.4248	162.08	160	1.7791	1.7795	202.44
20	—	1.4422	164.07	170	1.8169	1.8172	206.72
30	1.4595	1.4602	166.11	180	1.8573	1.8577	211.35
40	1.4785	1.4784	168.57	190	1.9023	1.9030	216.50
50	1.4975	1.4977	170.33	200	1.9526	1.9542	222.30
60	1.5165	1.5170	172.57	210	2.015	2.0120	228.90
70	1.5364	1.5376	174.92	220	2.077	2.0792	236.55
80	1.5570	1.5583	177.27	230	2.158	2.1585	245.55
90	1.5802	1.5808	179.78	240	2.255	2.2555	256.60

\* The molecular weight was taken to be 113.76.

*Volumes of a gram and molecular volumes of liquid—(continued).*

Temp.	Volumes of a gram in c.c.		* Molecular volumes in c.c.	Temp.	Volumes of a gram in c.c.		* Molecular volumes in c.c.
	Observed.	From curve.			Observed.	From curve.	
100	1·6044	1·6036	182·43	250	2·380	2 3805	270·80
110	1·6293	1·6280	185·20	260	2·556	2·5560	290·75
120	1·6543	1·6540	188·16	270	2·871	2·8710	326·60
130	1·6810	1·6821	191·86	274	3·137	3·1370	356·85
140	1·7137	1·7122	194·78	276·8 (critical)	—	4·227†	480·8†

*Volumes of a gram and molecular volumes of saturated vapour.*

Temperature.	Volumes of a gram in c.c.				Molecular volumes in c.c.
	Pressure apparatus.	Sealed tube method.		From curves.	
		I.	II.		
90°			443	460	52400
100			339	337	38300
110			255	251	28600
120			194	191	21800
130			147·1	148	16800
140			117·0	117·2	13340
150			93·7	93·8	10620
160			75·3	75·8	8630
170			62·0	62·1	7060
180			51·6	51·1	5810
190		42·5	42·2	42·2	4800
200		34·8		34·8	3960
210	23·45	28·8		28·7	3270
220	23·91	23·8		23·8	2707
230	19·60	19·6		19·63	2234
240	16·07	16·08		16·07	1828
250	13·03	12·95		13·02	1481
260	10·31	10·26		10·31	1172
270	7·565	7·61		7·57	861
274	6·36	6·36		6·36	723
276·8 (critical)	—			4·227 †	480·8 †

\* The molecular weight was taken to be 113·76.

† By the method of Caillietet and Mathias, corrected for the slight curvature of the "diameter."

In the following table, the calculated densities are obtained from the formula

$$D_t = 0.3550 - 0.0004115t - 0.0000000592t^2.$$

The density at the critical point, calculated from this formula, is 0.2366; from the simpler formula

$$D_t = 0.3567 - 0.000433t,$$

it would be 0.2369. The difference is small, but would be considerable at the lowest temperatures.

Temperature.	Densities.		Mean densities.		
	Liquid.	Saturated vapour	Observed.	Calculated.	$\Delta \times 10^4$
0	0.7102	0.0000	0.3551	0.3550	-1
10	0.7019	0.0001	0.3510	0.3509	-1
20	0.6934	0.0002	0.3468	0.3468	0
30	0.6848	0.0002	0.3425	0.3426	+1
40	0.6764	0.0004	0.3384	0.3384	0
50	0.6677	0.0005	0.3342	0.3343	+1
60	0.6592	0.0008	0.3300	0.3301	+1
70	0.6504	0.0012	0.3258	0.3259	+1
80	0.6417	0.0016	0.3217	0.3217	0
90	0.6328	0.0022	0.3175	0.3175	0
100	0.6236	0.0030	0.3133	0.3132	-1
110	0.6143	0.0040	0.3091	0.3090	-1
120	0.6046	0.0052	0.3049	0.3047	-2
130	0.5945	0.0068	0.3006	0.3005	-1
140	0.5841	0.0085	0.2963	0.2962	-1
150	0.5732	0.0107	0.2919	0.2920	+1
160	0.5620	0.0132	0.2876	0.2877	+1
170	0.5503	0.0161	0.2832	0.2833	+1
180	0.5383	0.0196	0.2789	0.2790	+1
190	0.5255	0.0237	0.2746	0.2747	+1
200	0.5117	0.0287	0.2702	0.2703	+1
210	0.4970	0.0349	0.2659	0.2660	0
220	0.4810	0.0420	0.2615	0.2616	+1
230	0.4633	0.0509	0.2571	0.2573	+2
240	0.4434	0.0622	0.2528	0.2528	0
250	0.4199	0.0769	0.2484	0.2484	0
260	0.3912	0.0970	0.2441	0.2440	-1
270	0.3482	0.1322	0.2402	0.2396	-6
274	0.3187	0.1574	0.2380	0.2378	-2
276.8 (critical)	—	—	—	0.2366	—

#### THEORETICAL CONCLUSIONS.

The absolute temperatures and the molecular volumes of the two hydrocarbons, both as liquid and as saturated vapour, were read from the curves at the usual series of "reduced pressures"; from these data,

the ratios of the temperatures and volumes to the critical constants were calculated, also the ratios of the actual to the theoretical densities of saturated vapour. For the sake of comparison, the ratios for normal and isopentane, normal hexane, and normal octane are added.

Reduced pressures.	Pressures.		Absolute temperatures.		Molecular volumes.			
					Liquid.		Saturated vapour.	
	Diiso-propyl.	Diiso-butyl.	Diiso-propyl.	Diiso-butyl.	Diiso-propyl.	Diiso-butyl.	Diiso-propyl.	Diiso-butyl.
0.000590	—	11.0	—	280.25	—	161.55	—	—
0.001474	34.40	27.5	258.2	296.25	—	164.75	—	—
0.002949	68.85	55.0	270.85	310.45	—	167.64	—	—
0.005898	137.7	110.05	285.4	326.2	128.37	171.06	—	—
0.011795	275.4	220.1	302.2	343.75	131.38	175.08	—	—
0.022411	523.2	418.2	319.3	362.5	134.75	179.64	—	—
0.044232	1033	825.4	341.2	386.1	139.26	185.79	19750	26900
0.088465	2065	1651	366.75	412.25	145.71	194.52	10130	13520
0.14744	3442	2751	388.5	434.95	152.07	203.25	6085	8290
0.20642	4819	3852	404.35	451.85	157.58	210.80	4330	5940
0.29488	6884	5502	422.95	471.25	165.05	221.25	2979	4090
0.44232	10326	8254	446.0	495.3	177.60	238.55	1888	2580
0.58978	13768	11005	464.25	513.5	191.60	257.40	1314	1811
0.73721	17210	13755	479.05	528.4	208.75	280.65	957	1312
0.82568	19275	15405	486.9	536.3	223.15	300.00	786	1067
0.88465	20650	16505	491.75	541.15	236.80	317.95	679	984
0.94863	22030	17610	496.15	545.75	255.75	344.80	572	773
0.97313	22715	18160	498.45	548.0	273.75	—	505	—
1.00000	23345	18660	500.4	549.8	356.0	480.8	356.0	480.8

Reduced pressures.	Volume of saturated vapour.						Densities of saturated vapour.					
	Critical volume.						Theoretical density.					
	iso-Pentane.	n-Pentane.	Diisopropyl.	n-Hexane.	Diisobutyl.	n-Octane.	iso-Pentane.	n-Pentane.	Diisopropyl.	n-Hexane.	Diisobutyl.	n-Octane.
0.044232	53.4	54.3	55.5	55.9	56.0	56.1	1.070	1.069	1.040	1.069	1.080	1.099
0.088465	27.7	28.4	28.4	29.1	28.2	29.3	1.111	1.098	1.089	1.103	1.148	1.128
0.14744	16.9	17.0	17.1	17.6	17.3	17.9	1.159	1.166	1.163	1.163	1.185	1.187
0.20642	12.0	12.1	12.2	12.4	12.4	12.7	1.215	1.217	1.204	1.218	1.228	1.218
0.29488	8.29	8.35	8.37	8.48	8.50	8.67	1.289	1.294	1.282	1.302	1.302	1.300
0.44232	5.27	5.27	5.30	5.36	5.37	5.43	1.427	1.489	1.421	1.445	1.446	1.452
0.58978	3.69	3.68	3.69	3.78	3.77	3.79	1.588	1.610	1.595	1.621	1.601	1.617
0.73721	2.65	2.68	2.69	2.69	2.73	2.73	1.825	1.826	1.807	1.851	1.819	1.852
0.82568	2.19	2.21	2.21	2.22	2.22	2.23	2.007	2.010	1.996	2.084	2.028	2.040
0.88465	1.80	1.90	1.91	1.92	1.92	—	2.186	2.204	2.180	2.219	2.213	—
0.94863	1.58	1.59	1.61	1.60	1.61	—	2.468	2.484	2.450	2.517	2.493	—
0.97313	1.39	1.40	1.42	1.41	1.40	—	2.754	2.759	2.698	2.774	—	—
1.00000	1.00	1.00	1.00	1.00	1.00	1.00	3.733	3.762	3.742	3.831	3.808	3.863



From the foregoing tables, it will be seen that the ratios of (*a*), the absolute temperatures to the absolute critical temperatures, (*c*) the volumes of saturated vapour to the critical volumes, (*d*) the actual to the theoretical densities, are higher for the normal paraffins than for their isomerides; the exceptions are slight, and are mostly near the critical points; including the cases where the ratios are equal, there are only 4 exceptions out of 51 comparisons under *a*, 6 out of 33 under *c*, and 8 out of 36 under *d*. On the other hand, the ratios (*b*) of the volumes of liquid to the critical volumes are lower for the normal paraffins than for the corresponding *iso*- or *diiso*-compounds; the exceptions are very slight, and only number 3 out of 44.

Comparing methyl butyrate with methyl *isobutyrate*, the ratios *a*, *b*, and *c* show differences in the same direction as above (exceptions, 4 out of 18, 0 out of 18, and 0 out of 12 respectively), but the ratios of the actual to the theoretical densities exhibit great irregularity, only 6 out of 13 being higher for the normal than for the *isobutyrate*.

We may therefore conclude, with regard to the ratios *a*, *b*, and *c*, that the statements made above represent general laws, but in the case of the ratios *d* the differences are too small, compared with the experimental errors, to allow of any very certain deduction being drawn.

Lastly, it may be interesting to compare the critical and some other constants of the same six hydrocarbons, in order to obtain some light on the relative influence of the single and double *iso*-groups.

Name.	B. p. 760 mm.	$\Delta$	Sp. gr. $\frac{D_4^{20}}{4}$	$\Delta$	Crit. temp.	$\Delta$
<i>iso</i> Pentane . . .	27.95°		0.63930		187.8°	
Normal pentane	36.3	-8.35°	0.64539	-0.00609	197.2	-9.4
<i>Diisopropyl</i> . .	58.1		0.67948		227.4	
Normal hexane.	68.95	-10.85	0.67697	+0.00251	234.8	-7.4
<i>Diisobutyl</i> . . .	109.2		0.71021		276.8	
Normal octane .	125.8	-14.6	0.71848	-0.00827	296.2	-19.4

Name.	Crit. pressure.	$\Delta$	Crit. density.	$\Delta$	$\frac{D_c^*}{D_c}$	$\Delta$
<i>iso</i> Pentane . . .	25020		0.2343		3.732	
Normal pentane	25100	-80	0.2323	+0.0020	3.762	-0.030
<i>Diisopropyl</i> . .	23345		0.2411		3.742	
Normal hexane.	22510	+835	0.2344	+0.0067	3.831	-0.089
<i>Diisobutyl</i> . . .	18660		0.2366		3.808	
Normal octane .	18730	-70	0.2327	+0.0039	3.863	-0.049

$\frac{*D_c}{D_c}$  = the ratio of the actual to the theoretical density at the critical point.

Comparing the *diisobutyl* and normal octane differences with those of normal and *isopentane*, it will be seen that the double *iso*-group has, in most cases, approximately twice the effect of the single in altering the properties. Whilst, however, the specific gravity at 0° and the critical pressure of the isomeride are in each case lower than those of the normal paraffin, the difference between the influence of the *iso*- and *diiso*-groups is here slight.

A comparison of the constants for methyl *isobutyrate* and methyl butyrate shows that the differences are the same in sign, and not very different in amount from those existing in the case of the pentanes.

As regards *diisopropyl* and normal hexane, it appears evident that something beyond the mere presence of the *diiso*-group in the former substance must be taken into account, for in the comparison of their differences with those of the pentanes (or octanes), great irregularities are to be observed. Thus, the critical pressure and the specific gravity of *diisopropyl* are both higher than those of normal hexane, instead of lower. It is somewhat remarkable that the critical densities of the *iso*- and *diiso*-compounds are in all four cases higher than those of the normal substances, but this peculiarity is greatly accentuated with *diisopropyl*.

From the difficulty experienced in preparing this hydrocarbon, it would seem that the  $(\text{CH}_2)_2\text{CH}-$  groups show considerably less tendency to unite together than those alkyl groups which are not of the form  $\begin{smallmatrix} \text{R} \\ \text{R}' \end{smallmatrix} > \text{CH}-$ . Thus, when potassium *isovalerate* was electrolysed, the amount of *diisobutyl* formed was very large compared with that of *isobutyl isovalerate*; whereas, under similar conditions, potassium *isobutyrate* gave a relatively much larger yield of *isopropyl isobutyrate* than of *diisopropyl*.

It seems probable that the peculiarities of *diisopropyl* may, in some way, be due to the fact that there are two CH groups attached to one another in the molecule.

In conclusion, we desire to thank the Government Grant Committee of the Royal Society for a grant by means of which the cost of the material and apparatus employed in this research was defrayed.

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# CIV.—*Vapour Pressures, Specific Volumes, and Critical Constants of Normal Octane.*

By SYDNEY YOUNG, D.Sc., F.R.S.

THE normal octane employed for this investigation was obtained from Kahlbaum, who prepared it from octyl iodide.

It was shaken five times with strong sulphuric acid, four times with a mixture of strong sulphuric and nitric acids, and five times again with strong sulphuric acid; it was then treated with caustic soda, washed with water, and dried with phosphoric oxide. On distillation, the greater part came over between 125 and 126° (corr. to 760 mm.), and after four fractionations with a twelve-column Young and Thomas dephlegmator a large amount was obtained with a constant boiling point (125·8° at 760 mm.). To make sure of the purity of the hydrocarbon, it was collected in three fractions, and the specific gravity of each was determined at 0° in a Sprengel tube of the form recommended by Perkin. The weighings are all reduced to a vacuum.

Fraction.	Temperature.	Specific gravity.
A .....	0°/4°	0·71850
B .....	0°/4°	0·71847
C .....	0°/4°	0·71848
B .....	17·75°/4°	0·70425

Thorpe (Trans. 1880, 37, 77) gives 125·46° and 0·71883 for the boiling point and specific gravity, but his specimen, which had been prepared by Schorlemmer from methylhexylcarbinol, did not boil very constantly (125·3—126·8°).

The three fractions were mixed together, and the boiling point was determined at various times with the following results :

Pressure.	Temperature.	Corr. to 760 mm.
756·0	125·6°	125·8°
748·65	125·3	125·85
741·0	124·85	125·75
756·7	125·65	125·8

Mean..... 125·8

The value of  $dp/dt$  at the boiling point = 21·1 mm. per degree. The boiling point, calculated from the constants for Biot's formula, is 125·6°.

The vapour pressures from 2 to 140 mm. were determined by Ramsay and Young's method, and from 160 mm. to the atmospheric pressure with a modified distillation bulb provided with a reflux condenser.

*Vapour pressures at low temperatures.*

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
2.25 mm.	-3.3°	10.3 mm.	19.7°	76.35 mm.	59.9°	322.8 mm.	97.35°
3.15	+1.2	12.35	23.15	96.65	65.6	355.4	100.4
3.95	4.4	15.3	26.75	116.6	70.0	391.0	103.4
4.9	8.2	18.1	29.65	136.45	73.95	429.4	106.4
5.35	9.25	21.7	33.25	157.15	77.3	469.8	109.85
5.5	9.55	26.6	37.3	179.1	80.8	516.8	112.4
6.15	11.2	31.45	40.45	205.0	84.3	566.9	115.55
6.65	12.55	39.2	44.95	230.3	87.75	616.4	118.55
7.45	14.35	49.65	50.1	259.7	91.15	668.6	121.4
8.6	17.05	61.85	55.2	289.5	94.25	730.4	124.55

The vapour pressures at high temperatures were determined with the pressure apparatus employed in previous researches. The observed pressures, together with those read from the curves constructed from the observations at low temperatures, and also the pressures calculated by means of Biot's formula  $\log p = a + ba^t + c\beta^t$  are given in the table below. The constants for Biot's formula are as follows:

$$\begin{aligned}
 a &= -0.89075 \\
 b &= 4.268604 \quad \log b = 0.6302859 \\
 c &= -2.628358 \quad \log c = 0.4196845 \\
 \log a &= 0.0240039 \\
 \log \beta &= 1.7195426 \\
 t &= t^\circ C - 10
 \end{aligned}$$

*Vapour pressures.*

Temp.	Pressures in mm.			Temp.	Pressures in mm.	
	Dynamical from curve.	Statical.	Calculated.		Statical.	Calculated.
0°	2.94	—	2.90	160°	1807	1802.4
10	5.62	—	5.62	170	2255	2249.0
20	10.45	—	10.35	180	2776	2775.4
30	18.40	—	18.21	190	3382	3390.7
40	30.85	—	30.71	200	4099	4105.0
50	49.35	—	49.33	210	4927	4928.9
60	77.55	—	78.10	220	5873	5874.6
70	117.9	—	118.55	230	6948	6955.0
80	174.8	—	174.8	240	8219	8184.5
90	253.5	—	251.0	250	9612	9578.8
100	353.6	—	351.95	260	11185	11156
110	481.9	—	482.8	270	12980	12937
120	646.4	—	649.3	280	15015	14942
130	—	859	859.4	290	17126	17198
140	—	1114	1114.5	296.2	18730	18734
150	—	1425	1426.9	(critical)		

The differences between the calculated and observed pressures near the critical point are greater than with most of the substances examined, thus at  $280^{\circ}$  the difference is  $-73$  mm., corresponding to  $+0.35^{\circ}$ , and at  $290^{\circ}$  it is  $+71$  mm., or  $0.3^{\circ}$ . Similar differences were, however, observed with stannic chloride and acetic acid. In all three cases the critical temperatures are higher than  $280^{\circ}$ , and the vapour of a liquid boiling at a higher temperature than bromonaphthalene (mercury with stannic chloride, dibenzylketone with acetic acid, and benzophenone with normal octane) was employed to heat the tube; in each case the calculated pressures from  $240^{\circ}$  or  $250^{\circ}$  to  $280^{\circ}$  are lower than the observed, but above  $280^{\circ}$  they are higher.

This points to an error in the temperature scale, and it is probable that the boiling point of bromonaphthalene was estimated somewhat too low by Dr. Ramsay and myself, owing, partly at any rate, to Regnault's values of the vapour pressures of mercury having been employed in the calculations. This error in the boiling point of bromonaphthalene is hardly noticeable so long as the critical temperatures of the substances investigated do not exceed  $280^{\circ}$ , but when the critical temperature is higher and another jacketing liquid is employed, it becomes apparent.

*Volumes of a Gram of Liquid and of Saturated Vapour.*

These constants were determined by the methods employed in previous researches. As before, the atomic weights given in F. W. Clarke's "Constants of Nature," Part V., taking that of hydrogen as unity, are adopted; the molecular weight of octane is therefore taken to be 113.76.

*Volumes of a gram and molecular volumes of liquid.*

Temp.	Volumes of a gram in c.c.		Molecular volumes in c.c.	Temp.	Volumes of a gram in c.c.		Molecular volumes in c.c.
	Observed.	From curves.			Observed.	From curve.	
$0^{\circ}$	1.3918	1.3918	153.34	$160^{\circ}$	1.7326	1.7326	197.10
10	—	1.4080	160.17	170	1.7646	1.7647	200.75
20	—	1.4240	161.99	180	1.8003	1.8000	204.75
30	1.4424	1.4405	163.87	190	1.8380	1.8380	209.10
40	1.4577	1.4577	165.83	200	1.8815	1.8808	213.95
50	1.4761	1.4754	167.84	210	1.9280	1.9270	219.20
60	1.4952	1.4939	169.95	220	1.9790	1.9790	225.15
70	1.5122	1.5127	172.08	230	2.0395	2.0405	232.15

*Volumes of a gram and molecular volumes of liquid—(continued).*

Temp.	Volumes of a gram in c.c.		Molecular volumes in c.c.	Temp.	Volumes of a gram in c.c.		Molecular volumes in c.c.
	Observed.	From curves.			Observed.	From curve.	
80	1.5812	1.5326	174.35	240	2.1180	2.1135	240.45
90	1.5520	1.5532	176.69	250	2.1995	2.1960	249.75
100	1.5748	1.5745	179.11	260	2.2975	2.2950	261.10
110	1.5971	1.5975	181.73	270	2.4300	2.4250	275.90
120	1.6203	1.6214	184.45	280	2.6280	2.6190	298.00
130	1.6484	1.6472	187.39	290	2.9510*	2.9720	338.10
140	1.6755	1.6741	190.45	296.2	—	4.297†	488.9†
150	1.7017	1.7021	193.63	(critical)			

*Volumes of a gram and molecular volumes of saturated vapour.*

Temperature.	Volumes of a gram in c.c.				Molecular volumes in c.c.
	Pressure apparatus.	Sealed tube method.		From curve.	
		I.	II.		
120°		304		303	34400
130		230		233	26500
140		182		183	20800
150		146		145	16500
160		116.1		116.5	13300
170		93.7		93.9	10670
180		75.8		76.1	8660
190		61.7	60.6	62.2	7080
200		50.7	51.4	51.1	5810
210		41.85	42.4	42.3	4810
220			35.1	34.8	3960
230			28.8	28.7	3270
240	23.40		23.4	23.6	2685
250	19.39		19.35	19.54	2230
260	16.06		15.95	16.07	1828
270	12.86		12.86	12.96	1474
280	10.10		10.06	10.17	1157
290	7.60 *			7.43	845
296.2 (critical)				4.297 †	488.9 †

\* At 289.85°.

† By the method of Cailletet and Mathias, allowing for the slight curvature of the "diameter."

The rather large differences between the smoothed and observed volumes of both liquid and of saturated vapour at the highest temperature are due to the alteration of the temperature scale in accordance with Biot's formula for vapour pressures. It is also to be noticed that between  $280^{\circ}$  and the critical temperature,  $296\cdot2^{\circ}$ , only one determination of volume was made. The curves above  $280^{\circ}$  are therefore of little value, especially as the alteration of form is so rapid near the critical point. The vapour pressure curve, however, shows no such change of form near the critical point, and the number of observations in that case is sufficient. Again the critical volume, being calculated from the critical density which is ascertained by the method of Cailletet and Mathias, is not rendered doubtful by the small number of observations near the critical point.

In calculating the critical density the slight curvature of the "diameter" was taken into account. The densities of liquid and of saturated vapour, the mean densities, and those calculated from the formula

$$D_t = 0\cdot3592 - 0\cdot0003986t - 0\cdot000000096t^2,*$$

are given in the table on p. 1150.

The densities of saturated vapour at and below  $120^{\circ}$  were calculated from the vapour pressures on the assumption that the vapour densities are normal.

The density at the critical point, calculated from the above formula, is  $0\cdot2327$ ; from the simpler formula

$$D_t = 0\cdot3634 - 0\cdot00044t$$

it would be  $0\cdot2331$ . The difference,  $0\cdot0004$ , is small, but at the lowest temperatures it would be considerable, amounting to  $0\cdot0042$  at  $0^{\circ}$ .

#### *Critical Constants.*

The critical constants are as follows :

Temperature .....	$296\cdot2^{\circ}$
Pressure .....	18730 mm.
Density .....	$0\cdot2327$
Volume of a gram.....	4·297 c.c.
Molecular volume .....	488·9 c.c.

\* These constants differ slightly from those given in a paper on the law of Cailletet and Mathias recently read before the Physical Society. The agreement between the calculated and observed mean densities is somewhat better with the new constants.

Temperature.	Densities.		Mean densities.		$\Delta \times 10^4$
	Liquid.	Saturated vapour.	Observed.	Calculated.	
0°	0·7185	0·0000	0·3592	0·3592	0
10	0·7102	0·0000	0·3551	0·3552	+1
20	0·7022	0·0001	0·3511	0·3512	+1
30	0·6942	0·0001	0·3471	0·3472	+1
40	0·6860	0·0002	0·3431	0·3431	0
50	0·6778	0·0003	0·3391	0·3390	-1
60	0·6694	0·0004	0·3349	0·3349	0
70	0·6611	0·0006	0·3308	0·3308	0
80	0·6525	0·0009	0·3267	0·3267	0
90	0·6438	0·0013	0·3226	0·3225	-1
100	0·6351	0·0017	0·3184	0·3184	0
110	0·6260	0·0023	0·3142	0·3142	0
120	0·6168	0·0033	0·3101	0·3100	-1
130	0·6071	0·0043	0·3057	0·3058	+1
140	0·5973	0·0055	0·3014	0·3015	+1
150	0·5875	0·0069	0·2972	0·2972	0
160	0·5772	0·0086	0·2929	0·2930	+1
170	0·5667	0·0107	0·2887	0·2887	0
180	0·5556	0·0132	0·2844	0·2843	-1
190	0·5441	0·0161	0·2801	0·2800	-1
200	0·5317	0·0196	0·2757	0·2756	-1
210	0·5189	0·0237	0·2713	0·2713	0
220	0·5053	0·0287	0·2670	0·2669	-1
230	0·4901	0·0348	0·2624	0·2624	0
240	0·4732	0·0424	0·2578	0·2580	+2
250	0·4554	0·0512	0·2533	0·2535	+2
260	0·4364	0·0622	0·2493	0·2491	-2
270	0·4123	0·0772	0·2448	0·2448	0
280	0·3818	0·0983	0·2401	0·2401	0
290	0·3365	0·1346	0·2356	0·2355	-1
296·2 (critical)	—	—	—	0·2327	

*Theoretical Conclusions.*

The absolute temperatures and the molecular volumes of liquid and saturated vapour were read from the curves at the usual series of "reduced pressures"; from these data, the ratios of the temperatures and volumes to the critical constants were calculated, also the ratios of the actual to the theoretical densities of saturated vapour (see table on p. 1151).

A comparison of these ratios with those of normal pentane, hexane and heptane confirms the conclusions previously reached that, for the members of a homologous series of paraffins, the ratios of the absolute temperatures at any series of corresponding pressures to the absolute critical temperatures, also the ratios of the actual to the theoretical densities at the critical points, increase slightly with rise of molecular

weight, whilst the ratios of the volumes of liquid at corresponding pressures to the critical volumes diminish slightly. The ratios of the volumes of saturated vapour to the critical volume differ very slightly from the corresponding ratios for normal heptane, and are on the whole very slightly lower; they are, however, higher than for normal hexane or pentane. It would appear then that, as a rule, these ratios increase with rise of molecular weight, but that the actual changes are too small, relatively to the experimental errors, to allow of a definite statement being made.

It is hoped that it may be possible to add a fifth member, butane, to the series of normal paraffins.

Reduced Pressure.	Pressure.	Absolute temperature.	Molecular volume.		Abs. Temp.	Vol. Liq.	Vol. Sat. Vap.	Density
			Liquid.	Saturated vapour.				
0.000590	11.05	294.0°	162.17	—	0.5165	0.3817	—	—
0.001474	27.60	310.9	165.39	—	0.5462	0.3883	—	—
0.002949	55.25	325.25	168.32	—	0.5714	0.3443	—	—
0.005898	110.5	341.25	171.73	—	0.5995	0.3513	—	—
0.011795	220.9	359.30	175.83	—	0.6313	0.3597	—	—
0.022411	419.8	378.5	180.51	—	0.6650	0.3698	—	—
0.044232	828.5	401.85	187.02	27400	0.7060	0.3826	56.1	1.099
0.088465	1657	429.4	195.84	14340	0.7544	0.4006	29.3	1.128
0.14744	2762	452.75	204.62	8730	0.7954	0.4186	17.9	1.167
0.20642	3866	469.85	212.39	6200	0.8255	0.4345	12.7	1.218
0.29488	5523	489.4	222.92	4240	0.8598	0.4560	8.67	1.300
0.44232	8285	513.75	241.11	2660	0.9026	0.4932	5.43	1.452
0.58978	11047	532.3	260.29	1851	0.9352	0.5324	3.79	1.617
0.73721	13810	547.5	284.40	1331	0.9619	0.5818	2.73	1.852
0.82568	15465	555.4	305.22	1089	0.9758	0.6243	2.23	2.049
0.88465	16570	560.35	—	—	0.9845	—	—	—
0.94363	17675	565.0	—	—	0.9926	—	—	—
0.97818	18225	567.2	—	—	0.9965	—	—	—
1.00000	18730	569.2	488.9	488.9	1.0000	1.0000	1.000	3.863

In conclusion, I wish to express my thanks to the Government Grant Committee of the Royal Society for a grant by means of which the cost of the material employed in this research was defrayed.

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CV.—*Separation of Neobornylamine from Bornylamine.*

By MARTIN ONSLOW FORSTER and JAMES HART-SMITH, A.R.C.S.

WHEN camphoroxime is reduced with sodium in boiling amyl alcohol, at least two bases are formed, of which the dextrorotatory bornylamine can be isolated by a simple process. The isomeric base, neobornylamine, although produced in some quantity, is purified with considerable difficulty, owing to the hydrochloride being more freely soluble than the corresponding salt of bornylamine; when first described, in fact, doubt was expressed as to whether the specimen examined could be regarded as quite free from the dextrorotatory isomeride (Forster, Trans., 1898, 73, 391).

During an investigation of bornylamine derivatives conducted with the object of studying the effect on specific rotatory power produced by replacement of aminic hydrogen (Forster, Trans., 1899, 75, 934, 1149), a quantity of the base had been accumulated which, owing to admixture with a considerable proportion of neobornylamine, was quite unsuitable for the purpose in view. We have utilised this material in an attempt to decide two questions arising out of the change which camphoroxime undergoes when submitted to reduction. In the first place, it seemed not unlikely that other bases might be produced in addition to those mentioned, and we have therefore searched for dibornylamine, amylbornylamine, inactive bornylamine, and the corresponding derivatives of neobornylamine, but no evidence of the production of any one of these compounds has been obtained. The second object of this investigation was to ascertain the specific rotatory power of purified neobornylamine, and incidentally to devise a process by which that base could be isolated from mixtures containing a large portion of the isomeride.

In order to purify neobornylamine, it was necessary to find a derivative of the base which is less readily soluble than the corresponding derivative of bornylamine. Several salts of inorganic acids were first prepared, but in no case was the difference in solubility sufficiently great to admit of separating the two bases by fractional crystallisation of these derivatives. Equally unavailing was an attempt to purify the levorotatory compound by converting it into the salt of camphoroximeacetic acid, although the bornylamine salt is a well-defined substance. A better prospect of success was offered by the study of dibornylloxamide,  $C_{10}H_{17} \cdot NH \cdot CO \cdot CO \cdot NH \cdot C_{10}H_{17}$ , obtained by the action of ethyl oxalate on the base. This compound, unlike the derivatives of bornylamine hitherto examined, is more freely soluble than the corresponding derivative of the levorotatory base, and it is therefore possible to remove it completely from the



compound produced by the action of ethyl oxalate on neobornylamine, afterwards regenerating the last-named substance by hydrolysing the residue with alcoholic potash. By this method, we have obtained neobornylamine melting at  $184^{\circ}$ , and having, in alcohol, the specific rotatory power  $[\alpha]_D -43.7^{\circ}$  (compare *Trans.*, 1898, 73, 391). Unfortunately, however, for reasons which appear below, the process cannot be applied successfully to the treatment of mixtures containing a large proportion of the dextrorotatory base.

*Salts of Bornylamine.*

An examination of the following salts of bornylamine has established the conformity of this base to the well-known generalisation of Oudemans, according to which the molecular rotation of an optically active base is independent of the nature of the salt. This is apparent from the subjoined table :

	$[\alpha]_D$	$[\alpha]_D$ calculated for the base.
Hydrochloride .....	+23.2°	+28.7°
Hydrobromide .....	20.4	31.2
Hydriodide .....	16.0	29.4
Nitrate .....	21.0	29.6
Sulphate.....	21.3	28.1
Benzoate.....	17.1	30.7

The hydrochloride gave  $[\alpha]_D +23.2^{\circ}$  in a 2 per cent. solution in absolute alcohol and  $[\alpha]_D +21.7^{\circ}$  when dissolved in water. The aqueous solution is intensely bitter, and when moderately dilute, may be boiled without yielding the free base.

The *hydrobromide* is precipitated slowly when aqueous potassium bromide is added to the calculated amount of bornylamine hydrochloride dissolved in water. It is freely soluble in boiling water, crystallising in concentric aggregates of long, highly lustrous, slender needles; cold absolute alcohol dissolves it very readily. The salt does not melt below  $260^{\circ}$ , and the aqueous solution may be boiled without yielding the free base. A one per cent. solution in absolute alcohol gave  $[\alpha]_D +20.4^{\circ}$ .

The *hydriodide* is rapidly precipitated on mixing solutions of potassium iodide and bornylamine hydrochloride. A moderately concentrated solution in water yields the free base when boiled, but the salt may be dissolved in warm water, and crystallises from dilute solutions in long, flat, transparent prisms. A 3.5 per cent. solution in absolute alcohol gave  $[\alpha]_D +16.0^{\circ}$ .

The *nitrate* dissolves freely in boiling water, and crystallises from

the cooling liquid in radially disposed aggregates of silky, white needles, which frequently approach an inch in length; the salt melts and evolves gas at  $240^{\circ}$ . It dissolves readily in cold absolute alcohol, and does not dissociate when the aqueous solution is boiled. A 1.5 per cent. solution in absolute alcohol gave  $[\alpha]_D + 21.0^{\circ}$ .

The *sulphate* is sparingly soluble in cold water, and crystallises from boiling solutions in lustrous, white leaflets. A 2 per cent. solution in absolute alcohol gave  $[\alpha]_D + 21.3^{\circ}$ .

The *benzoate* crystallises from boiling water in long, silky, white needles and melts at  $178-179^{\circ}$ . A 2 per cent. solution in absolute alcohol gave  $[\alpha]_D + 17.1^{\circ}$ .

*Camphoroximeacetic acid*,  $C_{10}H_{16} \cdot NO \cdot CH_2 \cdot CO_2H$ .

One hundred grams of camphoroxime, dissolved in 500 c.c. of alcohol, were heated with 60 grams of chloroacetic acid, and 60 grams of caustic soda dissolved in a small quantity of water, in a reflux apparatus on the water-bath during 8 hours. A current of steam was then passed through the liquid, which, when free from alcohol, was acidified with dilute sulphuric acid, considerable excess being employed in order to redissolve any camphoroxime which had escaped conversion into acid. The precipitate, which at first was somewhat slimy, soon hardened, and was then filtered, washed, and redissolved in cold aqueous potassium carbonate; on acidifying the filtered solution with dilute hydrochloric acid, camphoroximeacetic acid was precipitated in lustrous, white leaflets.

The substance dissolves very readily in alcohol, and is also soluble in much boiling water, from which it crystallises in long, lustrous, flat needles, which become opaque in the desiccator. Twice recrystallised from petroleum, which deposits it in rosette-like aggregates, the acid melts at  $100-102^{\circ}$  and decomposes at  $200^{\circ}$ .

0.2876 gave 16.6 c.c. moist nitrogen at  $20^{\circ}$  and 757 mm.  $N = 6.56$ .

$C_{12}H_{19}O_3N$  requires  $N = 6.22$  per cent.

A solution containing 0.8460 gram in 25 c.c. of absolute alcohol at  $21^{\circ}$  gave  $\alpha_D - 24'$  in a 2 dcm. tube, whence the specific rotatory power  $[\alpha]_D - 5.9^{\circ}$ .

The *sodium* salt dissolves very readily in water and in alcohol, separating slowly from the latter in long, flat, transparent needles which become opaque at  $80^{\circ}$ . The specimen analysed was crystallised from water, which deposits it in silky, lustrous needles, and then dried in the desiccator:

0.2078 gave 0.0460  $Na_2SO_4$ .  $Na = 7.17$ .

1.0963 lost 0.2546  $H_2O$  during 15 hours at  $145-160^{\circ}$ .  $H_2O = 23.2$ .

$C_{12}H_{18}O_3 \cdot NNa \cdot 4H_2O$  requires  $Na = 7.21$ ;  $H_2O = 22.6$  per cent.

A 2 per cent. solution of the crystallised salt in absolute alcohol gave  $[\alpha]_D -10.5^\circ$ , corresponding to  $[\alpha]_D -13.4^\circ$  for the anhydrous substance. A 2 per cent. solution in water gave  $[\alpha]_D -24.2^\circ$  for the anhydrous salt.

The *bornylamine* salt is at once precipitated on mixing alcoholic solutions of bornylamine and camphoroximeacetic acid in molecular proportion. It is sparingly soluble in cold ethyl acetate, and crystallises from the hot solution in small, transparent prisms; it melts and evolves gas at  $208^\circ$ .

0.1656 gave 0.4258  $\text{CO}_2$  and 0.1524  $\text{H}_2\text{O}$ .  $\text{C}=70.12$ ;  $\text{H}=10.16$ .

$\text{C}_{12}\text{H}_{19}\text{O}_8\text{N}, \text{C}_{10}\text{H}_{19}\text{N}$  requires  $\text{C}=69.84$ ;  $\text{H}=10.05$  per cent.

A solution containing 0.3952 gram in 25 c.c. of absolute alcohol at  $21^\circ$  gave  $\alpha_D +6'$  in a 2 dm. tube, whence  $[\alpha]_D +3.16^\circ$ .

*Bornyloxamide*,  $\text{C}_{10}\text{H}_{17}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$ .

Ten grams of oxamethane were mixed with 14.5 grams of bornylamine and heated during 2 hours on the water-bath. At the end of this period, the mixture, which at first liquefied, had become solid, and was then dissolved in boiling ethyl acetate, which deposited minute needles melting at  $157^\circ$ ; a second crystallisation was without influence on the melting point and specific rotatory power.

0.1755 gave 0.4152  $\text{CO}_2$  and 0.1441  $\text{H}_2\text{O}$ .  $\text{C}=64.55$ ;  $\text{H}=9.12$ .

$\text{C}_{12}\text{H}_{20}\text{O}_2\text{N}_2$  requires  $\text{C}=64.27$ ;  $\text{H}=8.93$  per cent.

Bornyloxamide is sparingly soluble in boiling petroleum, from which it crystallises in lustrous needles melting at  $162^\circ$ . It is readily soluble in cold chloroform and in hot alcohol, crystallising from the latter in lustrous needles. The substance is somewhat soluble in boiling water, which deposits it in long, white needles on cooling. The specific rotatory power of a 2 per cent. solution in absolute alcohol is  $[\alpha]_D -24.1^\circ$ .

An attempt to prepare bornyloxamic acid,  $\text{C}_{10}\text{H}_{17}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , by the action of nitrous acid on bornyloxamide was unsuccessful. The substance is also indifferent towards benzoyl chloride, and does not give rise to a platinichloride.

*Dibornyloxamide*,  $\text{C}_{10}\text{H}_{17}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{17}$ .

15.3 grams of bornylamine were covered with 7.3 grams of ethyl oxalate, the mixture becoming warm. After being heated in a reflux apparatus during  $2\frac{1}{2}$  hours, a solid substance began to separate; the product was therefore transferred to a beaker, allowed to cool, and treated with a few c.c. of cold ethyl acetate, when it became crystal-

line. The compound was then drained, and redissolved in boiling ethyl acetate, which deposits it in prismatic crystals melting somewhat indefinitely at  $140^{\circ}$ .

0.1852 gave 0.4928  $\text{CO}_2$  and 0.1691  $\text{H}_2\text{O}$ .  $\text{C} = 72.57$ ;  $\text{H} = 10.14$ .

$\text{C}_{22}\text{H}_{30}\text{O}_2\text{N}_2$  requires  $\text{C} = 73.33$ ;  $\text{H} = 10.00$  per cent.

Dibornylloxamide is practically insoluble in boiling water, but dissolves very readily in chloroform; it is sparingly soluble in cold petroleum, dissolving more readily in the boiling liquid, from which it separates in lustrous leaflets. It dissolves in about 30 parts of absolute alcohol at  $16^{\circ}$ , and crystallises from this solvent in silky needles. The specific rotatory power in absolute alcohol is  $[\alpha]_{\text{D}} - 29.6^{\circ}$ .

*Attempts to separate Neobornylamine from Bornylamine.*

In the preparation of bornylamine by reducing camphoroxime with sodium and amyl alcohol, it has been customary to decompose the sodium amyloxide with hydrochloric acid, remove the amyl alcohol in a current of steam, and allow the acid liquid to cool; the crystals which then separate contain a preponderating amount of bornylamine hydrochloride, and therefore yield a dextrorotatory base on treatment with alkali, whilst the acid mother liquor deposits chiefly neobornylamine hydrochloride when evaporated. It is the base derived from this acid mother liquor which has been employed in the following experiments.

An impure specimen of neobornylamine, having  $[\alpha]_{\text{D}} - 25.4^{\circ}$ , was obtained in the manner indicated, and heated with ethyl oxalate ( $\frac{1}{2}$  mol.) during 3 hours. The product was then exhausted with a small quantity of boiling ethyl acetate, filtered, and recrystallised twice from that solvent; recrystallisation from petroleum followed by absolute alcohol yielded a substance which melted somewhat indefinitely at  $185-187^{\circ}$ , and gave  $[\alpha]_{\text{D}} - 60.7^{\circ}$  in a 1 per cent. solution in absolute alcohol. Further crystallisation failing to raise the specific rotatory power, a portion of the substance, which we were disposed to regard as pure di-neobornylloxamide, was hydrolysed with alcoholic potash. The base thus obtained melted at  $180^{\circ}$ , and gave  $[\alpha]_{\text{D}} - 31.1^{\circ}$ ; it therefore corresponded very closely with the specimen described in the first paper on this subject (Trans., 1898, 73, 386).

On comparing the solubility in absolute alcohol of dibornylloxamide with that of the foregoing derivative, it was found that the latter is appreciably less readily soluble, and we were therefore sanguine of having at length found a means of separating the two bases. Accordingly, 300 grams of the base obtained from the acid mother liquor were heated with 150 grams of ethyl oxalate in a reflux apparatus

during 5 hours. The product, when cold, being very viscous, was mixed with a small proportion of ethyl acetate, and this precipitated a white solid which, when filtered and drained on porous earthenware, weighed 175 grams. Extraction with 500 c.c. of boiling ethyl acetate removed a substance which crystallised from the cooling liquid in snow-white needles, melting and evolving gas at  $241^{\circ}$ ; more of this compound, which contained 7.8 per cent. of nitrogen, was obtained on extracting the residue with a further quantity of ethyl acetate, but the specific rotatory power being  $[\alpha]_D - 30.5^{\circ}$ , it was evidently a different substance from the one obtained in the first experiment. The residue, after being extracted repeatedly with boiling ethyl acetate until no more soluble matter could be removed, was hydrolysed with alcoholic potash, yielding a base which melts at  $184^{\circ}$ , and gives  $[\alpha]_D - 43.7^{\circ}$  in a 4 per cent. solution in absolute alcohol, and  $[\alpha]_D - 27.0^{\circ}$  in a benzene solution of the same concentration. We regard this substance as pure neobornylamine, but are unable to identify either the insoluble compound which yields it on hydrolysis, or the substance melting at  $241^{\circ}$ , because the base obtained on hydrolysing the latter derivative melts at  $176^{\circ}$ , and gives  $[\alpha]_D - 13.1^{\circ}$  in absolute alcohol, appearing therefore to be a mixture of bornylamine and neobornylamine.

It will be noticed that the specific rotatory power of neobornylamine, obtained by the method indicated, is  $12^{\circ}$  higher than that of the specimen prepared previously, and the hydrochloride of the purified base has  $[\alpha]_D - 44.2^{\circ}$  instead of  $[\alpha]_D - 39.0^{\circ}$ . It will not be necessary, however, to revise the description which has been already given of the crystalline acyl derivatives of the base. The acetyl compound, for instance, obtained from the specimen having the higher rotatory power, crystallises from petroleum in long, slender needles melting at  $144^{\circ}$  and having  $[\alpha]_D - 19.1^{\circ}$  in a 2 per cent. solution; moreover, this derivative, and the benzoyl compound, when hydrolysed, yield the base which gives  $[\alpha]_D - 43.7^{\circ}$ .

Having several grams of this material at our disposal, we converted a portion into the *benzylidene* derivative, which was obtained as a pale yellow, viscous oil boiling at  $180^{\circ}$  under 25 mm. pressure. The substance does not crystallise when cooled, or after a long interval, and its oily nature accounts for the fact that the specimen of benzylidenebornylamine obtained by Griepenkerl was liquid (*Annalen*, 1892, 269, 353), whilst the purified base is a crystalline solid (Forster, *Trans.*, 1899, 75, 1152). Benzylideneneobornylamine does not yield a crystalline methiodide when heated in a sealed tube with methyl iodide, and consequently it has not been possible to obtain methyl-neobornylamine from it.

It cannot be claimed that the process here indicated for isolating

neobornylamine is very successful, because it can be applied only to mixtures having a specific rotatory power not less than  $[\alpha]_D - 10^\circ$ , and therefore already rich in the levorotatory base. An attempt to deal with a mixture of approximately equal quantities of the two bases led to the isolation merely of two crystalline substances, which differ from those already described. The procedure was substantially the same as before, the product of the action of ethyl oxalate on the base being exhausted twelve times with 1000 c.c. of boiling ethyl acetate. The solid deposited by the first extract differed quite perceptibly from the eleven succeeding fractions, which approximated to one another in appearance, melting point, and specific rotatory power. It was therefore dealt with separately, being dissolved in boiling absolute alcohol, which deposited compact, transparent crystals with a small proportion of long, silky needles; the latter, being specifically light, were easily separated by mechanical means, and the remainder was then recrystallised until the specific rotatory power of two successive fractions was the same. The compound thus obtained appeared a perfectly definite substance, and analysis pointed to the empirical formula of dibornyl-oxamide:

0.1868 gave 0.5010  $\text{CO}_2$  and 0.1717  $\text{H}_2\text{O}$ .  $\text{C} = 73.14$ ;  $\text{H} = 10.21$ .

0.2624 ,, 18.4 c.c. of nitrogen at  $19^\circ$  and 760 mm.  $\text{N} = 8.23$ .

$\text{C}_{22}\text{H}_{36}\text{O}_2\text{N}_2$  requires  $\text{C} = 73.33$ ;  $\text{H} = 10.00$ ;  $\text{N} = 7.77$  per cent.

In spite of this result, however, the appearance and properties of the substance were totally distinct from those of dibornyl-oxamide. It crystallised from petroleum in well-formed, transparent prisms melting at  $100^\circ$ , instead of lustrous leaflets melting at  $140^\circ$ ; alcohol deposited it in large transparent crystals, which become opaque on exposure to air, instead of long, silky needles. Moreover, the specific rotatory power was higher, being  $[\alpha]_D - 36.4^\circ$  in a 4 per cent. solution in absolute alcohol. Yet, although these crystals had every characteristic of a definite substance, the base obtained on hydrolysis melted at  $164^\circ$ , and gave  $[\alpha]_D + 30.7^\circ$ .

The substance associated with the foregoing compound was isolated by recrystallising together all fractions subsequent to the first, until the melting point underwent no change. In this way, long, silky needles were obtained, melting and evolving gas at  $251^\circ$ . No conclusion regarding the composition of this compound could be drawn from analysis. Several concordant determinations of carbon gave nearly 4 per cent. less than the amount required by the formula for dibornyl-oxamide; the quantities of hydrogen and nitrogen, however, were in agreement with those required by that expression. In spite of this, the base obtained on hydrolysis was practically pure bornylamine.

Although several hundred grams of the mixture were manipulated

in one experiment, no derivative of neobornylamine could be isolated. The substance remaining undissolved after twelve successive extractions with 1000 c.c. of boiling ethyl acetate was not a definite compound, as the base resulting on hydrolysis gave  $[\alpha]_D + 23^\circ$ . We had therefore convinced ourselves that it is hopeless to deal by this method with mixtures of bornylamine and neobornylamine, unless the latter base preponderates considerably, and further experiments in this direction were therefore abandoned.

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CVI.—*Aminoamidines of the Naphthalene Series. (Third Communication on Anhydro-bases.)*

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THE azo-derivatives of ethenyltriaminonaphthalene were incidentally referred to in a former communication by one of the authors and Percy P. Phillips (*Trans.*, 1899, 75, 1016). In continuing the investigation of these compounds we had occasion to prepare some ethenyltriaminonaphthalene by the process of Markfeldt (*Ber.*, 1898, 31, 1174) for comparison with the original anhydro-base described in 1887 (Meldola and Streatfeild, *Trans.*, 51, 691). It was found to our surprise that the phenylazo-derivatives obtained from the bases by combination with phenyldiazonium salts were isomeric and not identical, and a further examination of the bases has revealed the fact that the isomerism of the azo-derivatives is due to the isomerism of the ethenyltriaminonaphthalenes which are not identical as assumed by Markfeldt in the paper referred to. This isomerism of the anhydro-bases is certainly unexpected, and is the more remarkable since they are both prepared from the same dinitroacetnaphthalide, the only difference being the nature of the reducing agent, Markfeldt having substituted iron and hydrochloric acid for tin and this acid, as originally employed in 1887. That the isomerism is entirely due to the nature of the reducing agent has been proved by repeated experiments with the same specimen of dinitroacetnaphthalide.

In the present communication, we give a detailed account of the results of our investigation of Markfeldt's base and some of its salts and azo-derivatives, so as to bring into prominence the differences between these and their isomerides obtained from the original ethenyltriaminonaphthalene of 1887. With respect to the nature of the

isomerism, we have come to the conclusion that it is most probably due to structural difference and not to space configuration (stereoisomerism), since the characters of the two sets of compounds are profoundly different. As was indicated in 1887, two constitutional formulæ are possible :



Which of these represents our original base and which Markfeldt's isomeride must for the present remain undecided. The main point established by the present research is that tin and iron behave differently as reducing agents towards 2:4-dinitro-1-acetnaphthalide. The constitution of the isomeric bases will form the subject of future investigation, and it is proposed to extend the study of the difference in the behaviour of the two metals as reducing agents to other nitro-compounds, since evidence has already been obtained that this peculiarity is not manifested only in the naphthalene series.

*Markfeldt's Ethenyltriaminonaphthalene,*



Meldola and Streatfeild's anhydro-base is so soluble in water that it has not yet been isolated (Trans., 1887, 51, 698). Markfeldt's base is much less soluble, and separates out as an oily resin on adding sodium hydroxide solution to a strong aqueous solution of the hydrochloride. The resinous mass becomes crystalline on standing, and the free base can be crystallised from hot water, in which it readily dissolves. The pure compound is probably white, but all our preparations consisted of flat, slate-coloured needles, the colour being no doubt the result of atmospheric oxidation. The melting point of the base, allowed to dry in air at the ordinary temperature, is 84—85°. On analysis :

0.1799 gave 0.4072 CO<sub>2</sub> and 0.1016 H<sub>2</sub>O. C = 61.73; H = 6.28.

0.1178 „ 17.95 c.c. moist nitrogen at 12.2° and 765 mm. N = 18.17.

0.2408, air-dried, lost 0.0354 H<sub>2</sub>O in water-oven. H<sub>2</sub>O = 14.70.

C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>·2H<sub>2</sub>O requires C = 61.80; H = 6.44; N = 18.03;

H<sub>2</sub>O = 15.45 per cent.

The water of crystallisation is not quite driven off at the temperature of the water-oven. The anhydrous base begins to soften and



shrink at  $128^{\circ}$  and fuses at  $135^{\circ}$ . Analyses of a specimen, dried as above, gave the following results:

0.1638 gave 0.4386  $\text{CO}_2$  and 0.0896  $\text{H}_2\text{O}$ .  $\text{C} = 73.03$ ;  $\text{H} = 6.08$ .

0.1112 „ 19.9 c.c. moist nitrogen at  $12.2^{\circ}$  and 773.7 mm.  $\text{N} = 21.58$ .

$\text{C}_{12}\text{H}_{11}\text{N}_3$  requires  $\text{C} = 73.10$ ;  $\text{H} = 5.58$ ;  $\text{N} = 21.32$  per cent.

This aminoamidine is more distinctly basic in character than its isomeride. It gives a precipitate with silver nitrate in ammoniacal solution, but it is not sufficiently acid to dissolve in aqueous sodium hydroxide. The silver salt is gelatinous, and could not be obtained pure enough for analysis.

#### *Salts of Markfeldt's Base.*

*Hydrochlorides.*—The salt prepared by Markfeldt's process, namely, by crystallisation in presence of excess of hydrochloric acid, is a dihydrochloride of the formula  $\text{C}_{12}\text{H}_{11}\text{N}_3 \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$ .

It consists of pinkish, flat, silky needles, the colour being doubtless the result of atmospheric oxidation. The specimen used for analysis was dried over lime in a desiccator, and had lost some hydrogen chloride under these conditions:

0.2435 gave 0.2322  $\text{AgCl}$ .  $\text{Cl} = 23.59$ .

0.1385 „ 17.05 c.c. moist nitrogen at  $11.8^{\circ}$  and 748.1 mm.  $\text{N} = 14.38$ .

$\text{C}_{12}\text{H}_{11}\text{N}_3 \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$  requires  $\text{Cl} = 24.65$ ;  $\text{N} = 14.58$  per cent.

The crystals become opaque on heating in the water-oven, and at  $150$ — $160^{\circ}$  (in an air-oven) the water and 1 mol. of hydrogen chloride are driven off, leaving a monohydrochloride:

0.210, dried over lime in a desiccator and heated at  $150$ — $160^{\circ}$  until constant in weight, lost  $0.0396 = 18.86$  per cent. The loss corresponding to  $\text{C}_{12}\text{H}_{11}\text{N}_3 \cdot 2\text{HCl} \cdot \text{H}_2\text{O} - (\text{HCl} + \text{H}_2\text{O}) = 18.92$  per cent.

The monohydrochloride can also be prepared from the dihydrochloride by the partial removal of hydrogen chloride by means of dilute cold aqueous ammonia. The first specimen prepared in this way was analysed under the impression that it was the free base, and the results showed that only half the acid is removed under these conditions:

0.2926 gave 0.6187  $\text{CO}_2$  and 0.1516  $\text{H}_2\text{O}$ .  $\text{C} = 57.67$ ;  $\text{H} = 5.76$ .

0.0886 „ 12.3 c.c. moist nitrogen at  $11^{\circ}$  and 766.2 mm.  $\text{N} = 16.67$ .

0.5503 „ 0.3260  $\text{AgCl}$ .  $\text{Cl} = 14.66$ .

The above specimen had been crystallised from water from which it separates as small, opaque, white needles melting at about  $282^{\circ}$  and

darkening with shrinkage from about  $265^{\circ}$ . This crystalline salt contains 1 mol. of water :

0.8020, dried in air, lost  $0.0535 \text{ H}_2\text{O}$  at  $150-160^{\circ}$ .  $\text{H}_2\text{O} = 6.67$ .  
 $\text{C}_{12}\text{H}_{11}\text{N}_3, \text{HCl}, \text{H}_2\text{O}$  requires  $\text{C} = 57.26$ ;  $\text{H} = 5.57$ ;  $\text{N} = 16.7$ ;  $\text{Cl} = 14.12$ ;  
 $\text{H}_2\text{O} = 7.16$  per cent.

The isomeric ethenyltriaminonaphthalene forms the hydrochlorides  $\text{C}_{12}\text{H}_{11}\text{N}_3, 2\text{HCl}, 1\frac{1}{2}\text{H}_2\text{O}$ ;  $\text{C}_{12}\text{H}_{11}\text{N}_3, 2\text{HCl}, 1\frac{1}{2}\text{H}_2\text{O}$ ;  $\text{C}_{12}\text{H}_{11}\text{N}_3, 2\text{HCl}$  (Meldola and Streatfeild, *loc. cit.*, 694—696).

*Sulphate*.—The sulphate differs from that of the isomeric base in being much more soluble in hot water. It crystallises from this solvent in small, flat, silky, white needles, becoming pink by atmospheric oxidation. A specimen dried over lime in a desiccator was analysed with the following results :

0.2192 gave  $23.75$  c.c. moist nitrogen at  $10.1^{\circ}$  and  $751.9$  mm.  $\text{N} = 12.81$ .  
 0.6691, dried in desiccator, lost  $0.0735 \text{ H}_2\text{O}$  in water-oven.  $\text{H}_2\text{O} = 10.98$ .  
 $\text{C}_{12}\text{H}_{11}\text{N}_3, \text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$  requires  $\text{N} = 12.69$ ;  $\text{H}_2\text{O} = 10.88$  per cent.

The anhydrous salt was also analysed :

0.3721 gave  $0.2926 \text{ BaSO}_4$ .  $\text{S} = 10.80$ .  
 0.2044 gave  $24.45$  c.c. moist nitrogen at  $10.2^{\circ}$  and  $767.1$  mm.  $\text{N} = 14.43$ .  
 $\text{C}_{12}\text{H}_{11}\text{N}_3, \text{H}_2\text{SO}_4$  requires  $\text{N} = 14.24$ ;  $\text{S} = 10.85$  per cent.

The isomeric sulphate retains  $\frac{1}{2}\text{H}_2\text{O}$  at  $220^{\circ}$  (Meldola and Streatfeild, *loc. cit.*, 692).

*Nitrate*.—This salt was prepared by dissolving the free base in dilute nitric acid. It crystallises from water in slender needles which soon become coloured by oxidation. A specimen dried in the water-oven was analysed with the following result :

0.0625 gave  $11.05$  c.c. moist nitrogen at  $9.8^{\circ}$  and  $754.8$  mm.  $\text{N} = 21.02$ .  
 $\text{C}_{12}\text{H}_{11}\text{N}_3, \text{HNO}_3, \frac{1}{2}\text{H}_2\text{O}$  requires  $\text{N} = 20.82$  per cent.

The salt could not be dried above the temperature of the water-oven without undergoing decomposition.

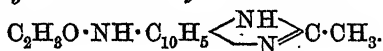
*Picrates*.—Hot alcoholic solutions of the base and of picric acid, when mixed and allowed to cool, deposit the picrate in the form of yellow, spherical nodules, a mode of crystallisation which is quite characteristic of this salt. After one crystallisation from alcohol, the salt was pure and had a softening point of about  $228^{\circ}$ , finally melting with decomposition at  $236^{\circ}$ .

0.0805 gave  $13.3$  c.c. moist nitrogen at  $11.7^{\circ}$  and  $755.8$  mm.  $\text{N} = 19.50$ .  
 $\text{C}_{12}\text{H}_{11}\text{N}_3, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$  requires  $\text{N} = 19.72$  per cent.

An attempt to prepare the picrate of the isomeric base showed that no definite compound with picric acid exists. On mixing aqueous

solutions of the hydrochloride of the base and of ammonium picrate, an ochreous, granular precipitate was obtained. The product separates from a hot saturated alcoholic solution in the form of resinous spherules giving no definite results on analysis. The compound could not be crystallised from any solvent, and it is probable that picric acid acts as an oxidising agent towards the base giving rise to indefinite products of decomposition.

*Acetyl Derivatives of the Isomeric Bases.*



A comparison of the acetyl derivatives of the two bases has shown that they differ considerably in their properties. The process of acetylation employed by Markfeldt (*loc. cit.*) may be applicable to his base, but even in this case we find that the prolonged boiling with excess of acetic anhydride is quite unnecessary. With our own base, this method, as already stated in a former paper (Meldola and Phillips, *loc. cit.*, 1012), is extremely destructive. The chief difference between the acetyl derivatives is the distinctly acid character of that derived from our base (*loc. cit.*, 1013). The isomeride obtained from Markfeldt's base is not acid enough to dissolve in aqueous alkali; it dissolves only in alcoholic alkali, and on the whole is more distinctly basic than acid. The acetyl derivative of Markfeldt's base has been so thoroughly investigated by that author that we have not thought it necessary to make any further examination of it beyond a comparison of certain salts.

The acetyl derivative of our anhydro-base is so difficult to obtain in a state of purity that we have not yet succeeded in getting very satisfactory analytical results. The difficulty of purification is due to the circumstance that the compound is both acid and basic in character, so that it forms salts with both acids and bases. The purest specimen hitherto prepared was obtained by dissolving the crude acetyl derivative in dilute alcoholic ammonia and exactly neutralising the warm solution with acetic acid. The compound separates on cooling in small, glistening, white scales grouped in rosettes. The melting point is about 281–284° with decomposition, Markfeldt's acetyl derivative having a melting point "above 280°" (*loc. cit.*, 1177):\*

0.1904 gave 0.4565 CO<sub>2</sub> and 0.0868 H<sub>2</sub>O. C = 65.39; H = 5.07.

0.0859 „ 12.25 c.c. moist nitrogen at 17.2° and 751.5 mm. N = 16.32.

C<sub>14</sub>H<sub>13</sub>ON<sub>3</sub>·H<sub>2</sub>O requires C = 65.37; H = 5.84; N = 16.34 per cent.

\* A specimen prepared by us, after crystallisation from water melted at about 286°, but began to shrink from about 270°.

The compound does not lose weight when heated to  $190^{\circ}$ , and the water of crystallisation could not be driven off without the substance undergoing decomposition. Other preparations in which a slight excess of acetic acid had unintentionally been employed for neutralising the alkaline solution gave on analysis indefinite results indicating mixtures of acetate with free acetyl derivative.

The *hydrochloride*,  $C_2H_5O \cdot NH \cdot C_{10}H_8 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{C} \cdot CH_3, HCl, H_2O$ , was prepared by dissolving the acetyl derivative in dilute hydrochloric acid, adding excess of strong hydrochloric acid, and allowing to crystallise. It separates in tufts of very small, white needles. A specimen dried at the ordinary temperature over lime in a desiccator was analysed with the following results:

0.1143 gave 14 c.c. moist nitrogen at  $15.7^{\circ}$  and 759.3 mm.  $N = 14.27$   
 0.1530 „ 0.0745 AgCl.  $Cl = 12.09$ .

$C_{14}H_{13}ON_3, HCl, H_2O$  requires  $N = 14.31$ ;  $Cl = 12.10$  per cent.

The water is not expelled at  $180^{\circ}$ , the loss at this temperature being 3.16 per cent., and the salt undergoing partial decomposition with discoloration.

An attempt to form a *picrate* showed that the acetyl derivative does not form a definite compound with picric acid. Nothing separates on mixing alcoholic solutions of the acetyl derivative and picric acid, and the product, which is thrown out on dilution with water, on continued crystallisation followed by analysis, gave indications of being a mixture rather than a definite compound. It is possible that, as in the case of the original anhydro-base, picric acid acts as an oxidising agent.

*Salts of the Acetyl Derivative of Markfeldt's Base.*—For comparison with the foregoing, the hydrochloride and picrate have been prepared from Markfeldt's base.

The *hydrochloride*,  $C_2H_5O \cdot NH \cdot C_{10}H_8 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{C} \cdot CH_3, HCl, H_2O$ , was prepared by dissolving the compound in dilute acid and then adding an equal volume of strong (fuming) acid. The salt crystallises in large, flat needles having a silvery lustre and becoming brownish on exposure to light and air. Analysis proved it to have the same composition as the isomeride.

0.1044 gave 13.15 c.c. moist nitrogen at  $17.2^{\circ}$  and 769.8 mm.  $N = 14.70$   
 0.0970 „ 0.0468 AgCl.  $Cl = 11.94$ .

$C_{14}H_{13}ON_3, HCl, H_2O$  requires  $N = 14.31$ ;  $Cl = 12.10$  per cent.

Heated at  $165^{\circ}$ , the salt becomes constant in weight and loses 5.53 per cent. of water. The whole of the water could not be expelled without decomposing the compound.

The *picrate* separates at once on mixing alcoholic solutions of the acetyl derivative and picric acid. It is a very definite compound consisting of slender, canary-yellow needles with a beautiful, silky lustre, melting with decomposition at  $287^{\circ}$ , and beginning to soften at  $281^{\circ}$ . The product used for analysis was purified by crystallisation from alcohol.

0.1380 gave 0.2610  $\text{CO}_2$  and 0.0448  $\text{H}_2\text{O}$ .  $\text{C} = 51.58$ ;  $\text{H} = 3.61$ .

0.1160 „ 17.5 c.c. moist nitrogen at  $14.4^{\circ}$  and 760.8 mm.  $\text{N} = 17.71$ .

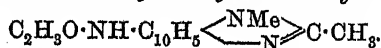
$\text{C}_{14}\text{H}_{15}\text{ON}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$  requires  $\text{C} = 51.28$ ;  $\text{H} = 3.42$ ;  $\text{N} = 17.95$  per cent.

### *Benzoyl Derivative of Markfeldt's Base.*

This compound was prepared from the hydrochloride by the method described by one of the authors and Percy P. Phillips last year (*loc. cit.*, 1015). It differs from its isomeride in being more distinctly crystalline, separating from alcohol in the form of dense, ochreous needles melting with decomposition at  $278$ – $280^{\circ}$ . It is less acid than its isomeride, being insoluble in aqueous alkali solutions.

With respect to the action of benzoyl chloride upon these aminoamidines, we may point out that if our view respecting the nature of the isomerism is correct, both compounds might be expected to yield 1 : 2 : 4-tribenzoyltriaminonaphthalene,  $\text{C}_{10}\text{H}_5(\text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5)_3$ , on treatment with this reagent in the presence of aqueous alkali, according to the well-known method of Schotten and Baumann. Experiments in this direction have been commenced, and will be resumed on some future occasion.

### *N-Methyl Derivative of Markfeldt's Acetyl Derivative,*



The acetyl derivative forms a gelatinous silver compound (Meldola and Phillips, *loc. cit.*, 1013), which becomes coherent, but non-crystalline, on standing for some time at a temperature just below the boiling point of the alcoholic solution. As the silver salt was amorphous, no attempt was made to analyse it, but the dry product was digested with methyl iodide in methyl alcohol and treated in the same way as described in the former paper relating to the isomeric compound from our aminoamidine of 1887.

This methyl derivative does not differ in any marked property from its isomeride. It is strongly basic in character and but slightly soluble in hot water. A specimen crystallised from dilute alcohol separated in rosettes of ochreous scales shrinking at  $250^{\circ}$  and melting with decomposition at about  $256^{\circ}$ .

0.1323 gave 17.6 c.c. moist nitrogen at 17.6° and 752.2 mm.  $N = 15.21$ .  
 $C_{15}H_{15}ON_3 \cdot H_2O$  requires  $N = 15.50$  per cent.

It therefore has the same formula as the isomeric compound. In attempting to determine the water, it was found that decomposition occurs at 155—160°, the loss of weight at this temperature being considerably in excess of that required for 1 mol.  $H_2O$ , namely, 13.72 instead of 6.6 per cent.

As we had only a small quantity of this compound at our disposal, the remainder was converted into the picrate which separates at once on mixing alcoholic solutions of the base and of picric acid. After one crystallisation from alcohol, it consists of long, slender, silky, yellow needles which fuse and decompose at 273° and begin to shrink and soften at 265—270°.

0.0794 gave 11.8 c.c. moist nitrogen at 16° and 760.3 mm.  $N = 17.31$ .  
 0.0602 " 8.85 " " 16° " 764.2 mm.  $N = 17.21$ .  
 $C_{15}H_{15}ON_3 \cdot C_6H_3O_7N_3$  requires  $N = 17.43$  per cent.

*Phenylazo-Derivatives*,  $C_6H_5 \cdot N_2 \cdot C_{10}H_4(NH_2) \begin{smallmatrix} <NH \\ >N \end{smallmatrix} C \cdot CH_3$ .

The first indication of the isomerism of the anhydro-bases was obtained on preparing a quantity of the phenylazo-derivative by the action of diazotised aniline upon the base in the presence of sodium acetate as described in the previous communication (*loc. cit.*, 1016). Some of Markfeldt's ethenyltriaminonaphthalene having been used for this purpose, it was found that the azo-compound was quite different in appearance and properties from that obtained last year. Instead of being violet and crystallising in bronzy scales almost insoluble in boiling alcohol, the new azo-derivative is red and fairly soluble in alcohol, crystallising from this solvent in brick-red, flat needles. If made to crystallise rapidly by stirring the solution on a watch glass, the small crystals appear bright red. By slow crystallisation from a large bulk of the solution, the compound separates in broad, scale-like needles which appear dull red with a slight metallic lustre when dry. It dissolves readily in toluene or chloroform with a fine red colour. Numerous analyses proved that this azo-derivative contains one mol. of water which can be expelled by heat or by crystallisation from a hydrocarbon with a high boiling point (toluene):

0.1986 gave 0.4928  $CO_2$  and 0.0981  $H_2O$ .  $C = 67.67$ ;  $H = 5.49$ .

0.1846 " 0.4593  $CO_2$  " 0.0874  $H_2O$ .  $C = 67.85$ ;  $H = 5.26$ .

0.0790 " 14.35 c.c. moist nitrogen at 8.6° and 765.1 mm.  $N = 22.01$ .

14.35 c.c. " " 9° " 750.5 mm.  $N = 21.93$ .

0.4070, dried at 140—150° until constant, lost 0.0241 H<sub>2</sub>O. H<sub>2</sub>O = 5.92. C<sub>18</sub>H<sub>15</sub>N<sub>5</sub>·H<sub>2</sub>O requires C = 67.71; H = 5.33; N = 21.94; H<sub>2</sub>O = 5.64 per cent.

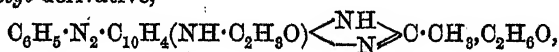
The anhydrous compound dried as above and another specimen crystallised from boiling toluene gave the following results:

0.1365 gave 0.3579 CO<sub>2</sub> and 0.0615 H<sub>2</sub>O. C = 71.51; H = 5.01.  
 0.2019 „ 0.5328 CO<sub>2</sub> „ 0.0909 H<sub>2</sub>O. C = 71.97; H = 5.00.  
 0.1899 „ 0.4976 CO<sub>2</sub> „ 0.0846 H<sub>2</sub>O. C = 71.46; H = 4.95.  
 0.1186 „ 23.1 c.c. moist nitrogen at 10.3° and 755.9 mm. N = 23.14.  
 0.1264 „ 24.35 „ „ 8.1° „ 751.4 mm. N = 22.97.

C<sub>18</sub>H<sub>15</sub>N<sub>5</sub> requires C = 71.76; H = 4.98; N = 23.26 per cent.

The azo-compound (hydrate) melts at 220—221°. It dissolves in alcoholic hydrochloric acid with a pale orange colour and a whitish hydrochloride separates out on standing. In alcoholic sodium hydroxide, the colour is not very different from that of the alcoholic solution, but more of an orange than red. When dissolved in glacial acetic acid and treated with sodium nitrite, an orange, crystalline substance is formed, which may be the acetoxy-derivative (Meldola and East, Trans., 1888, 53, 464) resulting from the replacement of the amino-group. The examination of this product is, however, not yet completed and its study will be resumed.

The *acetyl* derivative,



is best prepared by heating the azo-compound with acetic anhydride for about an hour on the water-bath. At the boiling point of acetic anhydride, decomposition is apt to occur. The product crystallises from alcohol in dense oblong tablets of a bright orange colour. The crystals contain alcohol of crystallisation:

0.3313 gave 0.8213 CO<sub>2</sub> and 0.1689 H<sub>2</sub>O. C = 67.61; H = 5.66.  
 0.1092 „ 16.7 c.c. moist nitrogen at 14.6° and 765.5 mm. N = 18.05.  
 0.1265 „ 19.2 „ „ 8.3° „ 750.9 mm. N = 18.06.  
 0.1659, dried at 150—155° until constant, lost 0.0203 C<sub>2</sub>H<sub>6</sub>O. C<sub>2</sub>H<sub>6</sub>O = 12.24.

C<sub>20</sub>H<sub>17</sub>ON<sub>5</sub>·C<sub>2</sub>H<sub>6</sub>O requires C = 67.87; H = 5.91; N = 17.99;  
 C<sub>2</sub>H<sub>6</sub>O = 11.83 per cent.

The compound free from alcohol gave the following results:

0.1244 gave 0.3182 CO<sub>2</sub> and 0.0548 H<sub>2</sub>O. C = 69.76; H = 4.89.  
 0.1522 „ 25.85 c.c. moist nitrogen at 8.6° and 761 mm. N = 20.46.  
 C<sub>20</sub>H<sub>17</sub>ON<sub>5</sub> requires C = 69.97; H = 4.96; N = 20.41 per cent.

The crystals of the acetyl derivative become opaque at 160—170°;

they darken at 240—250° and fuse with decomposition at about 253—254°. It is probable that decomposition begins much below the higher limit of temperature, as the loss on heating to determine the alcohol at 150—155° is over 1 per cent. in excess of that required by theory. Nitrogen is evolved, as already indicated, on boiling with acetic anhydride. The compound is completely reduced by zinc and hydrochloric acid in alcoholic solution, but the ethenyltetramino-naphthalene which might be expected to result is apparently very unstable and we have not yet succeeded in isolating it. With zinc dust and acetic acid in alcoholic solution, the acetyl derivative gives a hydrazo-compound crystallising in silvery scales and melting at about 245—250°, but this product requires further examination.

The isomeric phenylazo-derivative of our original anhydro-base has already been partially described (Meldola and Phillips, *loc. cit.*, 1016), and we are now enabled to give further details concerning this compound. The product crystallised from amyl alcohol or from a mixture of aniline and toluene contains, like its isomeride, 1 mol. of water:

0.0852 gave 0.2108 CO<sub>2</sub> and 0.04 H<sub>2</sub>O. C=67.48; H=5.21.

0.2114 „ 0.5267 CO<sub>2</sub> „ 0.0935 H<sub>2</sub>O. C=67.95; H=4.91.

0.0963 „ 18.75 c.c. moist nitrogen at 23.2° and 763 mm. N=21.98.

0.0884 „ 16.85 c.c. „ „ 15.6° „ 749.3 mm. N=21.92.

C<sub>18</sub>H<sub>15</sub>N<sub>5</sub>·H<sub>2</sub>O requires C=67.71; H=5.33; N=21.94 per cent.

The water in this azo-compound is not expelled so readily as that of the isomeride. At 150°, the loss is only about 0.5 per cent., but at 200—210° is greater than that required by theory, showing that decomposition occurs at the higher temperature.

The azo-compound is much less soluble in all solvents than the isomeride from Markfeldt's base. The solutions are dull red. It crystallises from amyl alcohol in dull, bronzy scales, and from aniline in dark violet needles with a dull, bronzy lustre. The melting point, as already stated, is between 257° and 260° with decomposition. The compound dissolves in strong sulphuric acid with an orange colour becoming red on dilution with water. In alcoholic hydrochloric acid, the colour is bright reddish-violet, the hydrochloride separating in small, bronzy needles on allowing the solution to stand. This property distinguishes the two isomeric compounds sharply from one another, the azo-derivative of Markfeldt's base dissolving in alcoholic hydrochloric acid with a pale orange colour and depositing a whitish hydrochloride on standing.

The hydrochloride of the azo-compound from our anhydro-base, prepared above, has the composition C<sub>18</sub>H<sub>15</sub>N<sub>5</sub>·HCl·H<sub>2</sub>O, as shown by



0.1201 gave 20 c.c. moist nitrogen at  $14.3^{\circ}$  and 764.7 mm.  $N = 19.66$ .  
 0.0682 „ 11.45 „ „ 12.5 „ 758.5 mm.  $N = 19.82$ .  
 0.1297 „ 0.0520 AgCl.  $Cl = 9.92$ .

$C_{18}H_{15}N_5, HCl, H_2O$  requires  $N = 19.69$ ;  $Cl = 9.99$  per cent.

The azo-compound can be acetylated in the same way as the isomeride, and gives an acetyl derivative which crystallises from alcohol in dense scales of a brown colour with glistening facets. The decomposing point is about  $252^{\circ}$ , and the compound begins to darken about  $240^{\circ}$ . Like its isomeride, it retains alcohol of crystallisation:

0.1166 gave 17.5 c.c. moist nitrogen at  $12.2^{\circ}$  and 772.3 mm.  $N = 18.07$ .  
 0.1253 „ 19 „ „ 16 „ 765.2 mm.  $N = 17.78$ .  
 0.1033, dried in water-oven and then at  $140-150^{\circ}$ , lost 0.0114  $C_2H_6O$ .  
 $C_2H_6O = 11.04$ .

$C_{20}H_{17}ON_5, C_2H_6O$  requires  $N = 17.99$ ;  $C_2H_6O = 11.83$  per cent.

The alcohol is thus not quite expelled at this temperature, and as at higher temperatures the compound showed signs of decomposing, the product was taken as free from alcohol and analysed:

0.0771 gave 13.6 c.c. moist nitrogen at  $19^{\circ}$  and 756.9 mm.  $N = 20.17$ .  
 $C_{20}H_{17}ON_5$  requires  $N = 20.41$  per cent.

The acetyl derivative is much less soluble than its isomeride, and could only be obtained in a satisfactory state of purity by crystallisation from ethyl alcohol, a very large volume of which is required. The acetylation of the azo-compound is best carried out by dissolving in glacial acetic acid and adding acetic anhydride to the solution. On warming on the water-bath, the violet colour of the solution changes to orange when the acetylation is complete. Boiling with acetic anhydride causes decomposition with the evolution of nitrogen and the formation of resinous products.

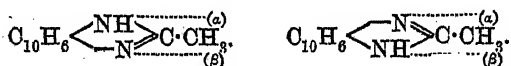
#### *p-Nitrophenylazo-derivative.*

Diazotised *p*-nitraniline combines readily with the aminoamidines, and a preliminary examination of the nitroazo-compound obtained from our original anhydro-base was made two years ago, but the investigation was interrupted in order to study the simpler phenylazo-compounds described in the present paper. The introduction of the nitro-group into the molecule modifies the properties of the compound by rendering it less stable, and the nitroazo-derivative appears to be decomposable by alkali with the formation of definite products. As this decomposition is likely to be of interest, we may place upon record the results thus far obtained, reserving for future investigation the nature of the products of the action of alkali upon the azo-compound.

On mixing solutions of diazotised *p*-nitraniline and the anhydro-base in the presence of sodium acetate in the usual way, the acetate of the nitroazo-compound separates as a dark violet, gelatinous precipitate, which dries to a bronzy powder. The compound has only been investigated qualitatively, as its insolubility has rendered it very difficult to obtain in a state of purity. It is distinctly acid in character, dissolving in aqueous and alcoholic sodium hydroxide with a magenta-red colour. It dissolves with a red colour in alcoholic hydrochloric acid, and to a slight extent in boiling fusel oil, nitrobenzene, or aniline. The colour of the solution in the last three solvents is indigo-blue, and it separates from nitrobenzene in small, coppery scales. The nitro-group is reducible by ammonium sulphide without the fission of the azo-group (Meldola, *Trans.*, 1883, 43, 425).

*Constitution of the Anhydro-bases and their Azo-derivatives.*

The constitution of the azo-derivatives cannot be definitely established until the nature of the isomerism of the anhydro-bases has been ascertained. On the view of the isomerism suggested at the commencement of this paper, the two bases should yield isomeric ethenyldiaminonaphthalenes on replacing the  $\text{NH}_2$  group by hydrogen :



It is possible, however, that one or the other of these isomerides is too unstable to exist, and becomes transformed by desmotropic change into the more stable form. This would appear to be the case if the ethenyldiaminonaphthalene of Prager (*Ber.*, 1885, 18, 2161) is identical with that of Liebermann and Jacobson (*Annalen*, 1882, 211, 67), and Fischer and Hepp (*Ber.*, 1887, 20, 1249, 1272). In the first method of preparation (Prager), the reducible nitro-group is in the  $\beta_1$ -position, whilst in the second method (Liebermann and Jacobson), the nitro-group is in the  $\alpha_1$ -position. It appears, however, that the anhydro-bases obtained by the two methods are identical (Beilstein, *Handbuch*, 3, 992), and, if so, it is most probable that the compound is susceptible of desmotropic change. It will be necessary to re-investigate this subject from the point of view of the discovery of the specific action of the reducing agent upon the nature of the product of reduction as made known in the present paper, and this subject will be taken in hand as soon as possible. A preliminary experiment may be described here, which appears to show that the replacement of the  $\text{NH}_2$  group in Markfeldt's base gives rise to the same ethenyldiaminonaphthalene as that already investigated by Prager, &c. Some of Markfeldt's base was diazotised with sodium nitrite in a fairly strong solution, and then treated with a large excess of abso-

lute alcohol in the usual way. The tarry product obtained after distilling off the alcohol was extracted with dilute sodium hydroxide solution, which dissolves out the amidine by virtue of the acid character of the NH group. The solution, on the addition of excess of hydrochloric acid, deposited a crystalline hydrochloride consisting of white needles, which were collected and purified further by a repetition of the same treatment. The product, washed with water and dried under a desiccator over lime, had the composition of a monohydrochloride :

0.110 gave 12.45 c.c. moist nitrogen at 18° and 751.4 mm.  $N = 12.91$ .

$C_{12}H_{10}N_2 \cdot HCl$  requires  $N = 12.81$  per cent.

The picrate, formed by mixing aqueous solutions of the hydrochloride and ammonium picrate, was obtained, after two crystallisations from alcohol, in the form of silky, orange-yellow needles :

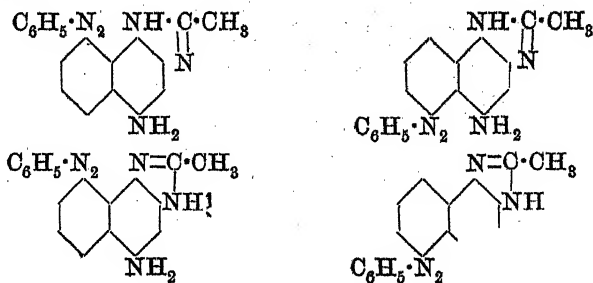
0.0968 gave 13.85 c.c. moist nitrogen at 13.6° and 764.3 mm.  $N = 16.94$ .

$C_{12}H_{10}N_2 \cdot C_6H_5O_7N_3$  requires  $N = 17.03$  per cent.

The melting point was 244°, the compound decomposing at about 255°. The melting point assigned to the picrate of Prager's base by Lellmann and Remy (*Ber.*, 1886, 19, 801) is 242°, so that the identity of our base with that of Prager appears to be established.

In view of possible desmotropy, it is still undecided whether in this amidine the NH group is in the  $\alpha$ - or  $\beta$ -position, hence the constitution of the base, so far as concerns the amidine ring, is open for investigation, and we give the above result simply as a preliminary step. The corresponding ethenyldiaminonaphthalene from our own anhydro-base will be prepared and described in a future communication.

Apart from the question of the configuration of the amidine ring, the position of the azo-group in the isomeric azo-compounds has yet to be determined. As the bases from which these compounds are derived are homonuclear tri-derivatives of naphthalene, it is most probable that the azo-derivatives are heteronuclear, the  $\alpha$ - or  $\beta$ -hydrogen atoms being in the most likely positions for substitution. On this view, the isomerism might be ascribed to such constitutional differences as the following :



Attempts to solve this problem experimentally have already been made, and the research will be continued in this direction. So far as the results go at present, we have only to state that each phenylazo-compound appears to be homogeneous, and not to consist of a mixture of isomerides. The constitution of the aminoamidine thus determines with absolute sharpness the position entered by the azo-group.

We have pleasure in acknowledging the assistance received from the Research Fund of the Chemical Society, from which a grant was made for the purchase of the materials required for the investigation. We are indebted also for some of the products to Messrs. Read Holliday and Sons, Limited, of Huddersfield. During the early part of the research we received much assistance from Mr. Elkan Wechsler, to whom we desire to express our thanks.

FINSBURY TECHNICAL COLLEGE.

## CVII.—*Note on the Elimination of a Nitro-group during Diazotisation.*

By RAPHAEL MELDOLA and ELKAN WECHSLER.

THE nitration of orthoacetanisidide, as described in a former note (Proc., 1898, 14, 226), gives rise to a mixture of two isomerides which can be separated by hydrolysing and repeatedly crystallising the mixed nitroanisidines from water. The mixed mononitroacetyl derivatives can also be further nitrated by dissolving in glacial acetic acid, adding fuming nitric acid in excess and allowing the solution to stand for twenty-four hours in the cold. The product after being precipitated by water and crystallised repeatedly from dilute alcohol consists of pale yellow needles of a dinitroacetanisidide melting at 162—163°.

0.1129 gave 15.6 c.c. moist nitrogen at 13° and 771.3 mm.  $N = 16.54$ .

0.1245 „ 17.75 „ „ 12.4° „ 746 mm.  $N = 16.56$ .

$C_9H_9O_6N_3$  requires  $N = 16.47$  per cent.

This dinitro-compound is easily hydrolysed by boiling for a few minutes with alcoholic soda. The dinitroanisidine thus obtained after precipitation by water and crystallisation from dilute alcohol, forms bright orange needles melting at 186—188°.

0.1252 gave 20.75 c.c. moist nitrogen at 14.2° and 773.9 mm.  $N = 19.82$ .

0.1371 „ 17.55 c.c. „ „ 10° „ 767 mm.  $N = 19.80$ .

$C_9H_7O_5N_3$  requires  $N = 19.72$  per cent.

The constitution of this dinitroanisidine has yet to be determined. It does not agree in properties with any of the known modifications; but since *p*-nitro-*o*-anisidine is one of the products of the nitration of acetanisidine (*Fabriques de Produits Chimiques de Thann et de Mulhouse*, Germ. Pat. 98637 of 1897; *Chem. Centr.*, 1898, ii, 950), it is probable that our compound results from the further nitration of this mono-nitro-derivative. In this case, the dinitro-compound may be the methyl ether of 3:5-dinitro-6-aminophenol. The amino-group in the dinitro-anisidine is readily diazotised by the usual methods. In our first experiments in which a somewhat dilute solution of the base in dilute sulphuric acid was treated with sodium nitrite, the diazo-salt did not separate out, but was precipitated in the form of yellow needles on the addition of alcohol and ether. It was afterwards found that by working in stronger solutions, or, still better, by diazotising with sodium nitrite in glacial acetic acid solution, good yields of the diazo-compound could be obtained at once. This compound is very stable and can be crystallised from boiling water or dilute alcohol. It consists of yellowish needles (from dilute solutions) or ochreous scales, which explode at about 178° and have all the properties of a true diazo-compound, combining at once with alkaline solutions of phenols to form colouring matters. Analysis indicated that one nitro-group is eliminated on diazotisation:

0.1277 gave 23.15 c.c. moist nitrogen at 10.3° and 752.4 mm.  $N = 21.43$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OCH}_3) \cdot \text{N}_2 \cdot \text{OH}$  requires  $N = 21.32$  per cent.

As we were unprepared for this result, confirmatory evidence was obtained by preparing the iodonitroanisole and the azo- $\beta$ -naphthol compounds, and the results leave no doubt that one nitro-group is eliminated. The diazo-compound is readily decomposed with the evolution of nitrogen on boiling with hydriodic acid and the iodo-derivative, after purification by crystallisation from dilute alcohol, forms flat, yellow needles, melting at 115–116°:

0.1741 gave 7 c.c. moist nitrogen at 11° and 775.2 mm.  $N = 4.88$ .

0.1119 „ 4.85 „ „ 12.5° „ 749.5 mm.  $N = 5.05$ .

$\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{I} \cdot \text{OCH}_3$  requires  $N = 5.01$  per cent.

On adding the diazo-compound to an alkaline solution of  $\beta$ -naphthol, a deep violet-black, gelatinous precipitate is at once formed. After being collected, washed with dilute acid, then with water, and finally with alcohol and dried, the azo-compound was purified by crystallisation from boiling aniline and obtained in the form of small, glistening, bronzy-green scales decomposing between 240° and 250°:

0.1208 gave 12.96 c.c. moist nitrogen at 10.6° and 753.7 mm.  $N = 12.68$ .

0.0883 „ 9.55 c.c. „ „ 10° „ 754.4 mm.  $N = 12.61$ .

$\text{NO}_2 \cdot \text{C}_9\text{H}_3(\text{OCH}_3) \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$  requires  $N = 13$  per cent.

The azo-compound is almost insoluble in alcohol and imparts a red colour to boiling glacial acetic acid. It dissolves in strong sulphuric acid with a violet colour, becoming orange on dilution with water. The solution in alcoholic sodium hydroxide is dull red, becoming more violet on warming with ammonium sulphide. This is in accordance with the view that the nitro-group occupies the para-position with respect to the azo-group.

The particular configuration of substituents which favours this easy displacement of the nitro-group by the action of nitrous acid can only be determined when the constitution of the dinitroanisidine has been established, and further experiments will be undertaken for this purpose. In the meantime, we have thought the broad fact sufficiently interesting to record in this preliminary notice. The elimination of a nitro-group from the phenylazo-derivative of methyl dinitrophenylacetate in the presence of alcoholic potash, as observed by Victor Meyer (*Ber.*, 1889, 22, 319) does not appear, at any rate, at first sight, to have any analogy with our observation, since the transformation of this azo-derivative is, in fact, a case of ring-formation with the production of a pyrazole derivative.

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### CVIII.—A Contribution to the Stereochemistry of Sulphur: an Optically Active Sulphine Base.

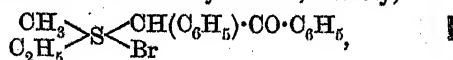
By SAMUEL SMILES, B.Sc.

FOR many years carbon was the only element known to give rise to optical activity in its compounds until Le Bel (*Compt. rend.*, 1891, 112, 724) obtained an optically active ammonium base by the fermentation of methylethylpropylisobutylammonium chloride, and later Pope and Peachey (*Trans.*, 1899, 75, 1127) obtained optically active methylallylphenylbenzylammonium iodide. In October, 1898, I commenced an investigation of the stereochemistry of sulphur, and some of the results were laid before the Society in December of the following year (*Proc.*, 1899, 15, 240; this vol., 160). The preparation of crystalline salts of methylethylthetine with certain optically active acids and bases was attempted, but without success. Profiting by the experience of Le Bel and Wedekind (*Zur Stereochemie des Stickstoffes*, 1899), attempts were also made to obtain sulphines containing asymmetric radicals, and it has been found that  $\alpha$ -bromacetophenone and benzoin react with the sulphides of the fatty series, forming sulphine bromides containing a phenacyl and a desyl group

respectively :  $\begin{array}{c} \text{R} \\ \text{R} \end{array} \text{S} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{Br} \end{array}$  and  $\begin{array}{c} \text{R} \\ \text{R} \end{array} \text{S} \begin{array}{c} \text{CH}(\text{C}_6\text{H}_5) \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{Br} \end{array}$ .

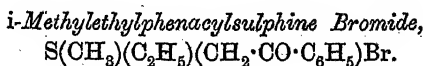
The investigation of these substances has been completed, and a paper describing the results obtained will shortly be laid before the Society. The sulphine bromide prepared from methyl ethyl sulphide and  $\omega$ -bromacetophenone,  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{CH}_3 \end{array} \text{S} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{Br} \end{array}$ , contains an asymmetric sulphur atom, and on account of its high molecular weight and comparative stability seemed more suitable for resolution into active components than any other sulphine base hitherto obtained. The salts of this sulphine, with the following acids, were therefore prepared, tartaric, malic, antimonyltartaric, camphoric, and orthomethyl camphoric ester, but were not obtained in the crystalline state. The great efficacy of the camphorsulphonic acids in resolving inactive bases into their optically active components had been pointed out by Pope, who applied them with brilliant success to asymmetric nitrogen (*loc. cit.*) and tin (Proc., 1900, 16, 42) compounds. He also prepared (Proc., 1900, 16, 12, 43) the *d*-camphorsulphonate and *d*- $\alpha$ -bromocamphorsulphonate of methylethylthetine, and found these salts to be crystalline, but was not successful in effecting a resolution of the base with their aid. Having exhausted all other easily obtainable active acids, I finally applied  $\alpha$ -bromocamphorsulphonic acid to the resolution of methylethylphenacylsulphine bromide and was successful, but, not wishing to interfere with Mr. Pope's work on this subject, I have refrained from publishing the results until he should have arrived at some definite conclusion in the matter. This has been attained (Pope and Peachey, this vol., 1072), and the following results are therefore laid before the Society, with Mr. Pope's acquiescence.

When methylethylphenacylsulphine bromide is treated in absolute alcoholic solution with the requisite amount of silver *d*-bromocamphorsulphonate, two salts are obtained, the less soluble having a molecular rotation of  $+250^\circ$  and the more soluble a rotation of  $+289^\circ$ . Since the molecular rotation of *d*-bromocamphorsulphonic acid in dilute aqueous solution is about  $+270^\circ$  (Walden, *Zeit. physikal. Chem.*, 1894, 15, 196), it is to be expected that the two salts should contain lævo- and dextro-base respectively. This was found to be the case, *l*- and *d*-picrates being obtained from the two bromocamphorsulphonates. The sulphine bromide produced by the interaction of methyl ethyl sulphide and bromodeoxybenzoin, namely,



contains both an asymmetric sulphur and carbon atom. It is therefore possible that the product should consist of two inactive stereo-

isomeric bromides, each of which should be separable into active components. However, when the above sulphine was examined by means of its picrate, it appeared to be homogeneous. It may be concluded that, in salts of sulphine bases, the four radicles which are directly united to the sulphur atom do not lie in the same plane with it, but are probably present in some tetrahedral arrangement,



Nineteen grams of bromacetophenone were added to 9 grams of methyl ethyl sulphide contained in a flask provided with a reflux condenser. Solution took place with absorption of heat, but in a short time the mixture became warm, and was cooled to prevent loss of sulphide. After standing overnight, the whole had solidified to a hard, colourless glass, which consisted of the almost pure sulphine bromide in nearly theoretical quantity, namely, 23 grams. The bromide is very soluble in alcohol, but only sparingly so in water, and is insoluble in ether. Many unsuccessful attempts were made to obtain it in the crystalline state.

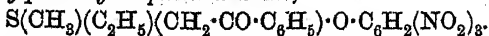
The *platinichloride* was precipitated as a light, buff-coloured powder on the addition of platinic chloride to the aqueous solution of the sulphine chloride; when purified, it melted at 173—174°. On analysis :

0.1848 gave 0.0448 Pt. Pt = 24.24.

0.2226 „ 0.0538 Pt. Pt = 24.17.

$(C_{11}H_{15}OSCl)_2PtCl_4$  requires Pt = 24.42 per cent.

*i*-Methylethylphenacylsulphine Picrate,



—The alcoholic solution of the bromide was treated with the requisite amount of picric acid dissolved in alcohol. After standing for a short time, the picrate was precipitated as a yellow, crystalline powder, very soluble in acetone, but insoluble in water. It is deposited from a mixture of acetone and alcohol as shining, yellow needles melting at 118—119°. On analysis :

0.2037 gave 19.05 c.c. of moist nitrogen at 26° and 764 mm. N = 10.4.

$C_{17}H_{17}O_8N_3S$  requires N = 9.93 per cent.

*d*- and *l*-Methylethylphenacylsulphine *d*-Bromocamphorsulphonate.

An alcoholic solution of methylethylphenacylsulphine bromide was boiled for a quarter of an hour with the calculated quantity of silver *d*-bromocamphorsulphonate in a flask provided with a reflux condenser. After rapidly removing the silver bromide by filtration, the



greater part of the alcohol was distilled off. The residue, on cooling, yielded an abundant crop of crystals.

By fractionally crystallising this from alcohol, a sparingly soluble salt, *l*-methylethylphenacylsulphine *d*-bromocamphorsulphonate, was easily obtained. It consisted of colourless needles very sparingly soluble in cold acetone and melting at 194—195°.

0.3695 gram dissolved in 25 c.c. of water gave  $\alpha + 1.47^\circ$  in a 2-decimetre tube at 19°, whence  $[\alpha]_D + 49.7^\circ$  and  $[M]_D + 251.0^\circ$ .

After further crystallisation, a specimen was obtained showing the following optical behaviour :

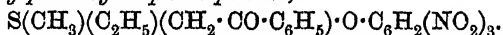
0.3186 gram dissolved in 25 c.c. of water gave  $\alpha + 1.26^\circ$  in a 2-decimetre tube at 20°, whence  $[\alpha]_D + 49.5^\circ$  and  $[M]_D + 250^\circ$ .

*d*-Methylethylphenacylsulphine *d*-bromocamphorsulphonate was contained in the alcoholic mother liquors, and was obtained therefrom as a white, crystalline precipitate, soluble in water and alcohol, but only sparingly so in cold acetone. It was deposited from acetone in fine silky needles melting at 183—184°. The purest specimen which could be obtained was examined in the polariscope with the following result :

0.4394 gram dissolved in 25 c.c. of water gave  $\alpha + 2.01^\circ$  in a 2-decimetre tube at 18°, whence  $[\alpha]_D + 57.2^\circ$  and  $[M]_D + 288.8^\circ$ .

These results point to the fact that the molecular rotation of the basic sulphine radicle in aqueous solution is approximately 20°.

*1-Methylethylphenacylsulphine picrate,*



—On adding the requisite amount of picric acid contained in saturated alcoholic solution to *l*-methylethylphenacylsulphine *d*-bromocamphorsulphonate, a yellow, crystalline precipitate was slowly formed. After allowing to stand for 2—3 hours, this was collected and recrystallised from acetone, being deposited in golden-yellow needles melting at 125°. When examined in the polariscope, it showed the following behaviour :

0.5168 gram dissolved in 25 c.c. of acetone gave  $\alpha - 0.38^\circ$  in a 2-decimetre tube, whence  $[\alpha]_D - 9.2^\circ$  and  $[M]_D - 38.9^\circ$ .

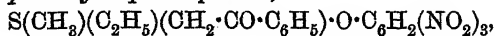
Another specimen showed the following rotation :

0.2988 gram dissolved in 10 c.c. of acetone gave  $\alpha - 0.28^\circ$  in a 1-decimetre tube, whence  $[\alpha]_D - 9.3^\circ$  and  $[M]_D - 39.3^\circ$ .

The following analytical results were obtained :

0.1590 gave 14.7 c.c. of moist nitrogen at 25° and 760 mm.  $N = 10.3$ .

$C_{17}H_{17}O_8N_3S$  requires  $N = 9.93$  per cent.

*d-Methylethylphenacylsulphine picrate,*

was prepared by precipitating the alcoholic solution of *d*-methylethylphenacylsulphine *d*-bromocamphorsulphonate with picric acid; it crystallised in bright yellow needles melting at 123—124°.

0.5411 gram dissolved in 25 c.c. of acetone gave  $\alpha + 0.31^\circ$  in a 2-decimetre tube, whence  $[\alpha]_D + 7.2^\circ$ .

A purer specimen showed the following behaviour:

0.1963 gram dissolved in 10 c.c. of acetone gave  $\alpha + 0.16^\circ$  in a 1-decimetre tube, whence  $[\alpha]_D + 8.1^\circ$  and  $[M]_D + 34.2^\circ$ .

On analysis the following numbers were obtained:

0.1872 gave 17.2 c.c. moist nitrogen at 23° and 760 mm.  $N = 10.3$ .

$\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}_3\text{S}$  requires  $N = 9.93$  per cent.

*Methylethylidesylsulphine Bromide, S(CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)(C<sub>14</sub>H<sub>11</sub>O)Br.*

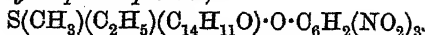
Bromodeoxybenzoin was dissolved in rather more than the theoretical amount of methyl ethyl sulphide. After standing for 24 hours, the mass had solidified, but it was found to be exceedingly difficult to obtain the sulphine bromide in a pure state from the product.

The *platinichloride* was prepared and, after purification, melted at 177° with decomposition. The following analytical results were obtained:

0.1257 gave 0.0258 Pt.  $\text{Pt} = 20.52$ .

0.1325 „ 0.0273 Pt.  $\text{Pt} = 20.60$ .

$(\text{C}_{17}\text{H}_{19}\text{SCl})_2\text{PtCl}_4$  requires  $\text{Pt} = 20.52$  per cent.

*Methylethylidesylsulphine picrate,*

—The somewhat impure bromide, prepared as just described, was completely converted into the picrate by means of a saturated alcoholic picric acid solution. A bright yellow, heavy, crystalline precipitate separated, which, on fractional recrystallisation from alcohol, appeared to be homogeneous. The pure picrate was deposited from alcohol as yellow leaflets melting at 162°.

The following analytical results were obtained:

0.1950 gave 15.1 c.c. of moist nitrogen at 25.5° and 763 mm.  $N = 8.6$ .

$\text{C}_{23}\text{H}_{21}\text{O}_3\text{N}_3\text{S}$  requires  $N = 8.4$  per cent.

In conclusion, I wish to express my indebtedness to R. Moritz,

B.Sc., for help afforded me in the preparation of the desylsulphines.

To Prof. Ramsay also my hearty thanks are due for much kind help and advice during this investigation.

UNIVERSITY COLLEGE, LONDON.

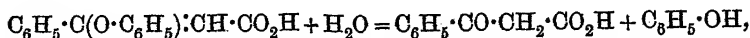
CIX.—*Condensation of Phenols with Esters of the Acetylene Series. Part III. Synthesis of Benzo- $\gamma$ -pyrone.*

By SIEGFRIED RUHEMANN and H. E. STAPLETON, Scholar of St. John's College, Oxford.

IN the previous papers (Ruhemann and Beddow, *Trans.*, 1900, 77, 984, 1119) on the interaction of phenols with the esters of the acetylene series, it was shown that, on using ethyl phenylpropiolate, the aryl ethers of ethyl  $\beta$ -hydroxycinnamate are produced, whilst the union of phenols with ethyl acetylenedicarboxylate yields the aryl ethers of ethyl hydroxyfumarate. It was also pointed out that, along with the latter esters, oils of high boiling point are obtained. We have now examined the product which accompanies the formation of ethyl phenoxyfumarate, and find that it is the result of a union of 2 mols. of phenol with 1 mol. of ethyl acetylenedicarboxylate. In the light of Michael's researches (Michael and Bucher, *Ber.*, 1895, 28, 2512; 1896, 29, 1792; see also Michael, *J. pr. Chem.*, 1899, [ii], 60, 106) on the behaviour of sodium ethoxide towards the same unsaturated ester, it may be concluded that the substance formed on using sodium phenolate has the constitution  $\text{CO}_2\text{Et} \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_5)_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , which characterises it as ethyl *as*-diphenoxysuccinate. A similar compound, ethyl *as*-dithiophenylsuccinate, is produced along with ethyl thiophenylfumarate by acting on sodium thiophenolate with ethyl acetylenedicarboxylate. Ethyl thiophenylfumarate is much less stable than ethyl phenoxyfumarate and its homologues, since, on hydrolysis, it is decomposed into oxalic and acetic acids on the one hand, and thiophenol on the other. The latter, however, is oxidised in the alkaline solution to phenyl disulphide,  $(\text{C}_6\text{H}_5\text{S})_2$ .

The investigation of the action between phenols and esters of the acetylene series has been extended by the authors of the present paper with the view of condensing the additive products to benzo- $\gamma$ -pyrone and its derivatives. We have attempted to accomplish this task by making use of concentrated sulphuric acid as a dehydrating

agent. With  $\beta$ -phenoxy-cinnamic acid, we find, however, that condensation to the phenyl derivative of benzo- $\gamma$ -pyrone, namely, flavone, does not occur, as the acid breaks up according to the equation,



yielding benzoylacetic acid and phenol, the latter, however, under the influence of the sulphuric acid, being transformed into its sulphonic acids. Phenoxyfumaric acid, on the other hand, being more stable, as has already been pointed out in the previous paper, partially undergoes the desired change and yields benzo- $\gamma$ -pyronemonocarboxylic acid. This acid, on distillation in a vacuum, loses carbon dioxide and benzo- $\gamma$ -pyrone,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{CH} \\ | \\ \text{O}-\text{CH} \end{smallmatrix}$ , the hitherto unknown parent sub-

stance of flavone and the yellow plant dyes such as chrysin, quercetin, and fisetin, is formed. The yield of the benzo- $\gamma$ -pyronemonocarboxylic acid is not very satisfactory, since phenoxyfumaric acid appears also to break up in a manner similar to  $\beta$ -phenoxy-cinnamic acid, with formation of the products of the decomposition of oxaloacetic acid, namely, oxalic and acetic acids.

#### EXPERIMENTAL.



The experiments previously described were exclusively directed to the study of the interaction between monohydric phenols and esters of the acetylene series, but we have now commenced to investigate the behaviour of dihydric phenols towards these esters. Up to the present we have examined the reaction of guaiacol with ethyl phenylpropionate. Their union is effected as in the former cases by dissolving sodium (1 at.) in an excess of hot guaiacol, adding the ester (1 mol.), and then warming the mixture until the sodium derivative of the phenol has dissolved. The viscous product on cooling sets to a solid mass; this is agitated with dilute sulphuric acid and ether, the ethereal layer freed from the dissolved guaiacol by shaking it with caustic potash, and the oil which remains after removing the ether by evaporation distilled in a vacuum. Ethyl  $\beta$ -o-methoxyphenoxy-cinnamate is a colourless, viscous oil with an aromatic odour, and boils at 230—231° under 15 mm. pressure. On analysis:

0.2038 gave 0.5437  $\text{CO}_2$  and 0.1122  $\text{H}_2\text{O}$ .  $\text{C}=72.75$ ;  $\text{H}=6.11$ .

$\text{C}_{18}\text{H}_{18}\text{O}_4$  requires  $\text{C}=72.48$ ;  $\text{H}=6.04$  per cent.

In its properties, the ester resembles the other aryl ethers of ethyl  $\beta$ -hydroxy-cinnamate. On boiling it with alcoholic potash for

1 hour on the water-bath, hydrolysis to the corresponding acid takes place.

*β*-*o*-Methoxyphenoxycinnamic acid,  $C_6H_5 \cdot C(O \cdot C_6H_4 \cdot O \cdot CH_3) : CH \cdot CO_2H$ , is precipitated from the alkaline solution by dilute sulphuric acid as a sticky product which gradually sets to a hard mass. This dissolves freely in alcohol, and the alcoholic solution, on dilution with water, gives an emulsion which, on standing, changes into colourless prisms. These begin to soften at  $120^\circ$ , and melt at  $138^\circ$  with evolution of gas. On analysis :

0.1914 gave 0.4985  $CO_2$  and 0.0907  $H_2O$ .  $C = 71.03$ ;  $H = 5.29$ .

$C_{16}H_{14}O_4$  requires  $C = 71.11$ ;  $H = 5.18$  per cent.

The solution of the acid in ammonia gives with silver nitrate a white precipitate of the silver salt which darkens at  $100^\circ$ .

*o*-Methoxyphenoxystyrene,  $C_6H_5 \cdot C(O \cdot C_6H_4 \cdot O \cdot CH_3) : CH_2$ , is obtained when the acid is heated, carbon dioxide being evolved. It distils at  $183^\circ$  under 15 mm. pressure as a colourless oil which solidifies after some time, and melts again at  $43-44^\circ$ . On analysis :

0.1642 gave 0.4800  $CO_2$  and 0.0910  $H_2O$ .  $C = 79.87$ ;  $H = 6.15$ .

$C_{15}H_{14}O_2$  requires  $C = 79.64$ ;  $H = 6.19$  per cent.

#### *Condensation of Thiophenol with Ethyl Phenylpropiolate and Ethyl Acetylenedicarboxylate.*

The action of thiophenol on the esters of the acetylene series resembles in every respect the behaviour of the phenols towards these compounds. The sodium thiophenolate required for the experiment is prepared by boiling a solution of thiophenol in toluene with sodium (1 at.) in a flask with a reflux condenser until the metal has disappeared and the precipitate is quite white. The required quantity of the ester (1 mol.) is then added, and the resulting product isolated in the same manner as are the corresponding phenoxy-compounds.

*Ethyl β-thiophenylcinnamate*,  $C_6H_5 \cdot C(S \cdot C_6H_5) : CH \cdot CO_2C_2H_5$ , is in this way formed from thiophenol and ethyl phenylpropiolate. After removal of the excess of thiophenol by shaking the product with caustic potash and then boiling off the toluene used in the reaction, it remains behind as an oil which rapidly solidifies. The ester is fairly soluble in ether, readily so in boiling alcohol, and crystallises from the latter in slightly yellow spangles which melt at  $95-96^\circ$ . On analysis :

0.1577 gave 0.4156  $CO_2$  and 0.0832  $H_2O$ .  $C = 71.87$ ;  $H = 5.86$ .

0.2324 „ 0.1927  $BaSO_4$ .  $S = 11.40$ .

$C_{17}H_{16}O_2S$  requires  $C = 71.83$ ;  $H = 5.63$ ;  $S = 11.27$  per cent.

*β-Thiophenylcinnamic acid*,  $C_6H_5 \cdot C(S \cdot C_6H_5) : CH \cdot CO_2H$ , is obtained by boiling the ester with alcoholic potash for 1 hour. After the alkaline solution has been freed from alcohol as completely as possible by distillation on the water-bath, water is added to the residue, and the solution acidified with sulphuric acid. The white precipitate, thus formed, is almost insoluble in water, but dissolves readily in ether or alcohol, and crystallises from the latter in colourless needles which melt at  $163^\circ$  with evolution of gas. On analysis:

0.1574 gave 0.4060  $CO_2$  and 0.0685  $H_2O$ .  $C = 70.34$ ;  $H = 4.83$ .

$C_{15}H_{12}O_2S$  requires  $C = 70.31$ ;  $H = 4.68$  per cent.

The solution of the acid in ammonia gives with copper sulphate a light green precipitate which does not blacken at  $100^\circ$ . On adding silver nitrate to the same solution, a white *silver* salt is formed, which decomposes when heated on the water-bath, but can be dried in a vacuum over sulphuric acid. On analysis:

0.3993 left on ignition 0.1193 Ag.  $Ag = 29.87$ .

$C_{15}H_{11}O_2SAg$  requires  $Ag = 29.75$  per cent.

*Thiophenylstyrene*,  $C_6H_5 \cdot C(S \cdot C_6H_5) : CH_2$ .

*β-Thiophenylcinnamic acid*, like the corresponding phenoxy-acid, on heating, loses carbon dioxide, and thiophenylstyrene is formed. It is a yellowish oil with a peculiar aromatic odour, boils at  $174-175^\circ$  under 14 mm. pressure, and has the density  $d_{28^\circ/28^\circ} 1.1024$ . On analysis:

0.1590 gave 0.4603  $CO_2$  and 0.0820  $H_2O$ .  $C = 78.95$ ;  $H = 5.73$ .

$C_{14}H_{12}S$  requires  $C = 79.24$ ;  $H = 5.66$  per cent.

Thiophenylstyrene, when heated with mineral acids, is decomposed, yielding only thiophenol and acetophenone.

*Ethyl Thiophenylfumarate*,  $CO_2C_2H_5 \cdot C(S \cdot C_6H_5) : CH \cdot CO_2C_2H_5$ .

The union of thiophenol with ethyl acetylenedicarboxylate takes place with development of heat, when the unsaturated ester (1 mol.) is carefully added to sodium thiophenolate (1 mol.) suspended in toluene. The oil which remains behind on treating the product of the reaction as in the former cases, is subjected to fractional distillation in a vacuum. The largest portion boils under 12 mm. pressure at  $201-202^\circ$ ; then the thermometer rises, and between  $220^\circ$  and  $260^\circ$  a very viscous substance passes over, which partially solidifies. The fraction of lower boiling point has a yellowish colour and its density  $d_{20^\circ/20^\circ} 1.1673$ . On analysis:

0.2010 gave 0.4437  $\text{CO}_2$  and 0.1090  $\text{H}_2\text{O}$ .  $\text{C} = 60.20$ ;  $\text{H} = 6.02$ .

$\text{C}_{14}\text{H}_{16}\text{O}_4\text{S}$  requires  $\text{C} = 60.0$ ;  $\text{H} = 5.71$  per cent.

The ester is most probably to be regarded as ethyl thiophenylfumarate, since it is formed in a manner similar to the additive product of phenol with ethyl acetylenedicarboxylate, which has been shown to be ethyl phenoxyfumarate. Ethyl thiophenylfumarate, as mentioned above, on boiling with alcoholic potash, breaks up and yields phenyl disulphide, the oxidation product of thiophenol. The alkaline liquor, after removal of the alcohol, does not give a precipitate with sulphuric acid. Ether extracts from the solution an oil which distills under diminished pressure, and, on standing, solidifies to a mass of colourless needles, which dissolve in alcohol and ether, and melt at  $60-61^\circ$ . The melting point, as well as the following analysis, prove the substance to be phenyl disulphide.

0.2037 gave 0.4924  $\text{CO}_2$  and 0.0880  $\text{H}_2\text{O}$ .  $\text{C} = 65.92$ ;  $\text{H} = 4.80$ .

$\text{C}_{12}\text{H}_{10}\text{S}_2$  requires  $\text{C} = 66.05$ ;  $\text{H} = 4.58$  per cent.

*Ethyl as-dithiophenylsuccinate*,  $\text{CO}_2\text{C}_2\text{H}_5 \cdot \text{C}(\text{S} \cdot \text{C}_6\text{H}_5)_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{C}_2\text{H}_5$ , is contained in the higher boiling portion of the product formed by the action of sodium thiophenolate on ethyl acetylenedicarboxylate. It is readily soluble in alcohol, fairly so in ether, and crystallises from the latter in large prisms which melt at  $82-83^\circ$ . On analysis:

0.2047 gave 0.4600  $\text{CO}_2$  and 0.1065  $\text{H}_2\text{O}$ .  $\text{C} = 61.29$ ;  $\text{H} = 5.78$ .

0.2157 „ 0.2548  $\text{BaSO}_4$ .  $\text{S} = 16.22$ .

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{S}_2$  requires  $\text{C} = 61.54$ .  $\text{H} = 5.63$ ;  $\text{S} = 16.41$  per cent.

*Ethyl as-diphenoxysuccinate*,  $\text{CO}_2\text{C}_2\text{H}_5 \cdot \text{C}(\text{O} \cdot \text{C}_6\text{H}_5)_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{C}_2\text{H}_5$ .—The fact that ethyl dithiophenylsuccinate accompanies the formation of ethyl thiophenylfumarate induced us to examine the portion of the oil of high boiling point which is formed by the action of sodium phenolate on ethyl acetylenedicarboxylate (compare this vol., 1121). By means of a careful fractional distillation, we were able to obtain a yellowish, viscous oil, which distilled at  $232-233^\circ$  under 15 mm. pressure, and, on analysis, gave numbers agreeing with those required for the above formula:

0.1778 gave 0.4395  $\text{CO}_2$  and 0.0963  $\text{H}_2\text{O}$ .  $\text{C} = 67.41$ ;  $\text{H} = 6.18$ .

$\text{C}_{20}\text{H}_{22}\text{O}_6$  requires  $\text{C} = 67.03$ ;  $\text{H} = 6.14$  per cent.

#### *Action of Sulphuric Acid on $\beta$ -Phenoxy-cinnamic Acid.*

$\beta$ -Phenoxy-cinnamic acid dissolves in concentrated sulphuric acid, with development of heat. After standing for 24 hours, water is gradually added while the solution is kept cool by a freezing mixture of ice and salt. A white precipitate is formed, and at the same time

the odour of acetophenone becomes perceptible. The solid crystallises from a mixture of benzene and light petroleum in colourless needles which melt at 103—104° with evolution of carbon dioxide, and yield acetophenone. These properties are characteristic of benzoylacetic acid, and the composition of the acid has been verified by the following analysis :

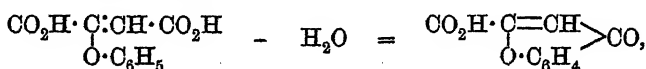
0.1842 gave 0.4455 CO<sub>2</sub> and 0.0850 H<sub>2</sub>O. C = 65.96 ; H = 5.12.

C<sub>9</sub>H<sub>8</sub>O<sub>3</sub> requires C = 65.85 ; H = 4.88 per cent.

Phenol, which must be regarded as the other product of this decomposition of  $\beta$ -phenoxyacinnamic acid, probably passes into solution as *o*- and *p*-phenolsulphonic acids.

*Action of Sulphuric Acid on Phenoxyfumaric Acid.*

We have previously mentioned that phenoxyfumaric acid differs from  $\beta$ -phenoxyacinnamic acid, inasmuch as sulphuric acid partially reacts with it according to the equation



and yields benzo- $\gamma$ -pyronecarboxylic acid. At the same time, a transformation takes place similar to that which the aryl ether of  $\beta$ -hydroxyacinnamic acid suffers, and there are formed, on the one hand, the products of the decomposition of oxaloacetic acid, namely, oxalic and acetic acids, and on the other, phenol, which, under the influence of the sulphuric acid, changes into its sulphonic acids.

*Benzo- $\gamma$ -pyronecarboxylic Acid.*—For the preparation of this substance, phenoxyfumaric acid is dissolved, at the ordinary temperature, in concentrated sulphuric acid, the solution allowed to stand overnight, and then gradually added to ice-cold water. Benzo- $\gamma$ -pyronecarboxylic acid is precipitated as a white solid which is sparingly soluble in water, but readily so in alcohol. It crystallises from the latter in colourless needles which melt and decompose at 250—251°. On analysis :

0.1948 gave 0.4508 CO<sub>2</sub> and 0.0606 H<sub>2</sub>O. C = 63.11 ; H = 3.45.

0.2012 „ 0.4638 CO<sub>2</sub> „ 0.0600 H<sub>2</sub>O. C = 62.86 ; H = 3.31.

C<sub>10</sub>H<sub>6</sub>O<sub>4</sub> requires C = 63.16 ; H = 3.16 per cent.

The acid dissolves in ammonia with great ease; on adding silver nitrate to the solution a *silver* salt is formed which is soluble in boiling water and crystallises from it in colourless needles. The salt contains 1 mol. H<sub>2</sub>O (which it does not lose at 110°), as shown by the following silver determinations :



0.2003 left on ignition 0.0686 Ag. Ag = 34.24.

0.2493     "     "     0.0858 Ag. Ag = 34.30.

$C_{10}H_5O_4Ag, H_2O$  requires Ag = 34.28 per cent.



On heating benzo- $\gamma$ -pyronecarboxylic acid in a vacuum, it loses carbon dioxide, and an oil passes over which, after a short time, sets to a solid. This dissolves with the greatest ease in ether, alcohol, chloroform, or benzene, but is less readily soluble in light petroleum (b. p. 70–80°), and crystallises from it in flat needles which melt at 59°. On analysis:

0.1190 gave 0.3230  $CO_2$  and 0.0455  $H_2O$ . C = 74.02; H = 4.25.

$C_9H_6O_2$  requires C = 73.97; H = 4.11 per cent.

Benzo- $\gamma$ -pyrone dissolves in cold concentrated sulphuric acid, and the yellowish solution shows a blue fluorescence.

We are continuing the study of benzo- $\gamma$ -pyrone, and propose to examine the action of sulphuric acid on the homologues of phenoxy-fumaric acid, in the hope of thus obtaining derivatives of benzo- $\gamma$ -pyrone with alkyl groups in the benzene nucleus.

GONVILLE AND CAIUS COLLEGE,  
CAMBRIDGE.

## CX.—Contributions to the Chemistry of Hydrotetrazines and Triazoles.

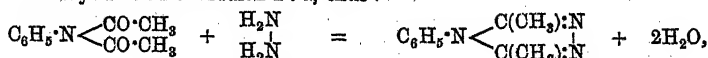
By OSWALD SILBERRAD, Ph.D.

In a paper, "Ueber die Polymerisationsproducte aus Diazoessig-ester," by Hantzsch and the author (*Ber.*, 1900, 33, 58), the synthesis of dihydrotetrazine was described and its constitution determined. The present paper deals with some of the derivatives of this substance.



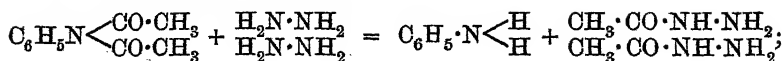
This base was first obtained by Pellizzari (*Atti R. Accad. Lincei*, 1899, [v], 8, 327). It is obtained, together with aniline, when diacetanilide and hydrazine hydrate in molecular proportion are heated together at 260° for 4 hours.\*

\* These two substances were heated together in an attempt to obtain 1-phenyl-2:5-dimethyl-1:3:4-triazadien-2:4, thus:



with a view to throwing light on the tautomeric character of the triazoles, a question which is now being investigated from a different standpoint.

The reaction may be explained thus :



the acetylhydrazine then undergoes condensation to dimethyldihydro-tetrazine.

The product was subjected to distillation. In the first fraction, collected below  $210^\circ$ , water, aniline, and traces of phenylhydrazine were detected. The second fraction, collected above  $260^\circ$ , solidified, and, on crystallisation from chloroform, yielded a substance melting at  $196^\circ$ , which proved on analysis to be dimethyldihydro-tetrazine.

Found C = 42.71 ; H = 7.22 ; N = 50.22 and 50.20.

$\text{C}_4\text{H}_8\text{N}_4$  requires C = 42.86 ; H = 7.14 ; N = 50.00 per cent.

Dimethyldihydro-tetrazine hydrochloride,  $\text{C}_4\text{H}_8\text{N}_4\cdot\text{HCl}$ , results on the addition of hydrochloric acid to an alcoholic solution of the base. It is very soluble in water, but less so in absolute alcohol, from which it crystallises in prismatic needles melting at  $232^\circ$ , with loss of hydrogen chloride.

Found N = 37.74 ; Cl = 24.00.

$\text{C}_4\text{H}_9\text{N}_4\text{Cl}$  requires N = 37.74 ; Cl = 23.85 per cent.

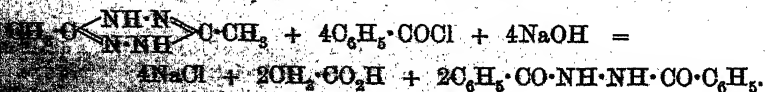
Sodium amalgam in alcoholic solution is without effect on the base ; with acetic acid and zinc dust, ethylhydrazine is not obtained (compare Hantzsch and Silberrad, *Ber.*, 1900, 33, 61), but after boiling, ether extracts from the filtrate, made alkaline with caustic soda, traces of a thick, oily substance, which has an odour resembling that of turpentine, resinifies immediately on exposure to air, and reduces Fehling's solution in the cold. Possibly this substance is dimethylhexahydro-tetrazine,  $\text{CH}_3\cdot\text{CH} \begin{smallmatrix} \text{NH}\cdot\text{NH} \\ \text{NH}\cdot\text{NH} \end{smallmatrix} \text{CH}\cdot\text{CH}_3$ , but it could not be obtained pure or in sufficient quantity for investigation.

*Action of Benzoyl Chloride.*—An aqueous solution of the base was shaken with an excess of benzoyl chloride and caustic soda solution in molecular proportion for 6 hours, excess of caustic soda was then added, and the mixture again shaken for a few hours. The crystalline product, after washing with water, ether, and crystallising from alcohol, melted at  $238^\circ$ , and proved to be *sym*-dibenzoylhydrazine.

Found C = 69.98 ; H = 5.16 ; N = 11.71.

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$  requires C = 70.00 ; H = 5.00 ; N = 11.67 per cent.

Acetic acid was readily detected in the alkaline mother liquor. The reaction may be expressed by the following equation :



3:5-Dimethyl-1:2:4-triazole,  $\text{CH}_3 \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{N} \\ \diagup \quad \diagdown \end{smallmatrix} \text{C} \cdot \text{CH}_3$ .

*Dimethyltriazole Nitrate*,  $\text{C}_4\text{H}_7\text{N}_3\text{HNO}_3$ .—To prepare this substance, a 5 per cent. solution of dimethyldihydrotetrazine is saturated at  $0^\circ$  with nitric oxides, and the resulting yellowish solution, after standing for a few hours, evaporated to dryness on the water-bath. The nitrate separates as a colourless, acid, very deliquescent, crystalline mass. It crystallises from water, in which it is very soluble, in colourless needles, and from absolute alcohol, in which it is less soluble, in shining leaflets, melts at  $125^\circ$ , and decomposes explosively on heating.

Found  $\text{N} = 35.22$ .  $\text{C}_4\text{H}_8\text{O}_5\text{N}_4$  requires  $\text{N} = 35.00$  per cent.

*Dimethyltriazole Hydrochloride*,  $\text{C}_4\text{H}_7\text{N}_3\text{HCl}$ , is readily obtained from the nitrate as follows. A concentrated solution is treated with excess of sodium ethoxide, filtered from the precipitated sodium nitrate, the excess of sodium ethoxide removed with excess of alcoholic hydrochloric acid, and the resulting solution evaporated to the crystallising point. On recrystallisation from a mixture of absolute alcohol and chloroform, the hydrochloride separates in indistinct needles or leaflets and melts at  $199^\circ$ . Traces of moisture lower its melting point in a very marked degree. The salt has an acid reaction, is exceedingly soluble in water and very hygroscopic. It was analysed with the following results:

Found  $\text{N} = 31.01$ ;  $\text{Cl} = 26.12$ .

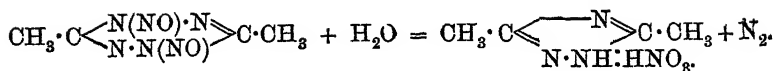
$\text{C}_4\text{H}_8\text{N}_3\text{Cl}$  requires  $\text{N} = 31.48$ ;  $\text{Cl} = 26.54$  per cent.

*Dimethyl-1:2:4-triazole* is obtained when the aqueous solution of the hydrochloride is treated with a slight excess of moist silver oxide and the solution evaporated in a vacuum. Evaporation on the water-bath brings about considerable loss owing to the volatility of the base. It is very soluble in water or absolute alcohol, less so in benzene or chloroform, from which it separates in colourless, prismatic needles, or shining leaflets, melting at  $142^\circ$  and boiling undecomposed at  $258^\circ$  under 752 mm. pressure.

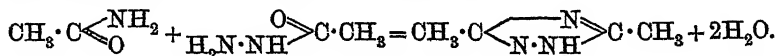
Found,  $\text{C} = 49.70$ ;  $\text{H} = 7.41$ ;  $\text{N} = 43.08$  and  $43.18$ .

$\text{C}_4\text{H}_7\text{N}_3$  requires  $\text{C} = 49.48$ ;  $\text{H} = 7.22$ ;  $\text{N} = 43.30$  per cent.

The formation of this substance by the method indicated is probably preceded by the production of dinitrosodimethyldihydrotetrazine,  $\text{CH}_3 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N}(\text{NO}) \\ \diagup \quad \diagdown \end{smallmatrix} \text{C} \cdot \text{CH}_3$ , indicated by the transient yellow coloration. This rapidly undergoes decomposition in the presence of water with the evolution of nitrogen and formation of the nitrate, thus:



Any doubt concerning the constitution of this body is removed by its synthesis from acetamide and acetylhydrazine, which condense on heating, as shown by the following equation:



When a mixture of acetamide and acetylhydrazine in molecular proportion, after heating to 220° for 4 hours, is subjected to distillation, dimethyl-1:2:4-triazole passes over to the extent of 90 per cent. of the theoretical between 255° and 260° under 754 mm. pressure. The product was identified by analysis (N=43.32 per cent.), melting point (142°), and analysis of its nitrate (N=35.18 per cent.), which melted at 125°.

*Silver Dimethyltriazole*,  $\text{C}_4\text{H}_6\text{N}_3\text{Ag}$ , is obtained as a white precipitate on adding silver nitrate to a mixture of ammonia and the base in molecular proportion. It is soluble in ammonia, nitric acid, or acetic acid, is fairly stable on exposure to light, and decomposes with evolution of cyanogen on heating.

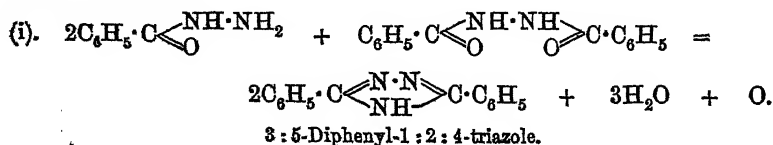
Found, N=20.41.  $\text{C}_4\text{H}_6\text{N}_3\text{Ag}$  requires N=20.62 per cent.

In all probability, this salt is a mixture of 4-silver-3:5-dimethyl-1:2:4-triazadien (1:2) and 1-silver-3:5-dimethyl-1:2:4-triazadien (2:4), as will be shown in a later communication.

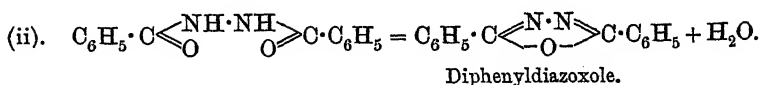
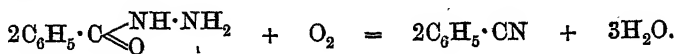


This substance was obtained by Pinner (*Ber.*, 1894, 27, 1006) by the action of hydrochloric acid on 3:6-diphenyl-1:2-dihydro-1:2:4:5-tetrazine,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{c} \text{N} \text{---} \text{N} \\ \text{NH} \cdot \text{NH} \end{array} \text{C} \cdot \text{C}_6\text{H}_5$ , and was termed diphenylisodihydrotetrazine by him. It is formed in small quantity, together with benzonitrile, diphenyltriazole, and diphenyldiazoxole (dibenzonylisoazoxime), which are the chief products, when benzoylhydrazine is heated at 260° for several hours.

The production of the last two compounds appears to be due to the intermediate formation of  $\alpha\beta$ -dibenzoylhydrazine, and may be expressed as follows:



To the liberation of oxygen the production of benzonitrile is evidently due, thus :



The isolation of the products was conducted as follows. Fifty grams of benzoylhydrazine were plunged into an air-bath at  $260^\circ$  and maintained at that temperature during several hours; if raised gradually to  $260^\circ$ , no diphenyldihydrotetrazine is produced. During this process, benzonitrile, together with traces of benzoic acid, distilled off, and was identified in the usual manner.

*Isolation of sym-3:6-Diphenyldihydrotetrazine.*—The non-volatile residue was finely powdered and extracted with warm 20 per cent. hydrochloric acid so long as anything dissolved. The solution was neutralised with ammonia, filtered, and the precipitate washed with ether and repeatedly crystallised from absolute alcohol. By this means, shining leaflets (0.5 gram) melting at  $263^\circ$  were obtained, which proved on analysis to be diphenyldihydrotetrazine.

Found C = 71.03. H = 5.29; N = 23.86.

$\text{C}_{14}\text{H}_{12}\text{N}_4$  requires C = 71.19; H = 5.08; N = 23.73 per cent.

*Isolation of 3:5-Diphenyl-1:2:4-triazole,*  $\text{C}_6\text{H}_5\cdot\text{C}\begin{array}{c} \text{N}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}\text{C}\begin{array}{c} \text{N}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}\text{C}_6\text{H}_5$ .

—The residue was well washed with ether to remove traces of benzoic acid, and then extracted with fairly dilute caustic soda solution so long as anything dissolved. The solution was then treated with a slight excess of dilute sulphuric acid, the precipitate washed with ether, and repeatedly crystallised from alcohol. By these means, flat, prismatic crystals melting at  $188^\circ$  were obtained, which proved on analysis to be hydrated diphenyltriazole. The yield amounted to 18 grams.

The substance lost 7.84 per cent.  $\text{H}_2\text{O}$  at  $100^\circ$ .

$\text{C}_{14}\text{H}_{11}\text{N}_3\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$  = 7.53 per cent.

The anhydrous product melted at  $192^\circ$ , and on analysis gave the following results :

Found C = 75.88; H = 5.32; N = 18.75.

$\text{C}_{14}\text{H}_{11}\text{N}_3$  requires C = 76.01; H = 4.98; N = 19.00 per cent.

*Isolation of Diphenyldiazoxole,*  $\text{C}_6\text{H}_5\cdot\text{C}\begin{array}{c} \text{N}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{array}\text{C}\begin{array}{c} \text{N}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{array}\text{C}_6\text{H}_5$ .—The residue, after extraction with caustic soda, was repeatedly crystallised

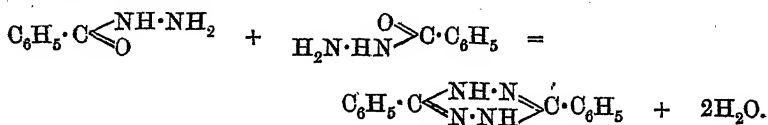
from absolute alcohol, whereby feathery needles melting at  $140^{\circ}$  were obtained, which, on analysis, proved to be diphenyldiazoxole; the yield amounted to 7.5 grams.

Found, C = 75.49; H = 4.80; N = 12.48.

$C_{14}H_{10}ON_2$  requires C = 75.68; H = 4.50; N = 12.61 per cent.

Diphenyldiazoxole sublimes on heating in beautiful, fern-like, branching needles.

*Synthesis of sym-3:6-Diphenyldihydrotetrazine.*—This substance may be obtained in theoretical quantity by heating benzoylhydrazine (3 parts) at  $230^{\circ}$  under such conditions that the formation of di-benzoylhydrazine cannot occur, namely, in the presence of excess of hydrazine hydrate (1 part).



The product, a colourless, crystalline mass, is freed from mother liquor and crystallised from absolute alcohol, from which it separates in colourless, nacreous leaflets, and melts at  $260^{\circ}$  (Pinner gives  $258^{\circ}$ ). The yield amounts to 96—97 per cent. of the theoretical:

Found, N = 23.70.  $C_{14}H_{12}N_4$  requires N = 23.73 per cent.

The aqueous mother liquor was found to contain ammonia, benzoic acid, and hydrazine hydrate, corresponding to 40 per cent. of that used.

#### *Action of Heat on aa-Benzoylphenylhydrazine.*

The effect of heat on *aa*-benzoylphenylhydrazine was studied with a view to the production of *sym*-1:3:4:6-tetraphenyldihydrotetrazine; the desired condensation, however, did not occur. One hundred grams of *aa*-benzoylphenylhydrazine were heated at  $260^{\circ}$  in an air-bath for 6 hours, during which operation ammonia was evolved and a faintly coloured, crystalline substance distilled over which proved to be a mixture of benzoic acid and benzophenone. The dark coloured non-volatile product was digested with benzene, the solution filtered from a black, insoluble residue, heated to boiling, treated with about twice its volume of boiling petroleum (b. p.  $140$ — $150^{\circ}$ ), and filtered while hot from a black, resinous substance. On cooling, a semi-crystalline, resinous mass separated; this was recrystallised from chloroform, dissolved in alcohol, and boiling water added to the solution, which was then filtered from a dark, resinous substance and allowed to cool until the substance which was separat-

ing was almost white and possessed a crystalline structure; the liquid was then rapidly filtered.

The solution, now almost colourless, was heated to boiling, hot water added until a slight permanent cloudiness existed, and then allowed to cool, when an almost colourless, crystalline compound melting at  $154^{\circ}$  separated. This was freed from mother liquor and recrystallised three or four times from absolute alcohol, then from benzene till its melting point rose to about  $160^{\circ}$ , and finally sublimed between watch glasses, whereby colourless, shining needles melting at  $162^{\circ}$  were obtained. These on analysis proved to be benzoylanilide, and not the desired tetraphenyldihydropyridazine.

Found, C = 79.34; H = 5.80; N = 7.23.

$C_{13}H_{11}ON$  requires C = 79.19; H = 5.58; N = 7.11 per cent.

The identity of this substance was further established by boiling it with hydrochloric acid, whereby it underwent hydrolysis with production of benzoic acid and aniline, which were identified in the usual manner.

An endeavour to produce tetraphenyldihydropyridazine on lines analogous to those so successful in the case of diphenyldihydropyridazine, namely, by heating  $\alpha\alpha$ -benzoylphenylhydrazine with phenylhydrazine, led to the same result. No traces of a body corresponding in any way to a tetraphenyldihydropyridazine could be detected. Mixtures of equal parts of  $\alpha\alpha$ -benzoylphenylhydrazine and phenylhydrazine heated at temperatures below  $230^{\circ}$  still contained unaltered benzoylphenylhydrazine, whilst at higher temperatures the decomposition products of the phenylhydrazine rendered the isolation of any compound even more tedious than that just described.

In conclusion, I wish to express my thanks to the Government Grant Committee of the Royal Society for pecuniary assistance, and to the Committee of the Davy-Faraday Laboratory of the Royal Institution for allowing me the use of the laboratory.

DAVY-FARADAY LABORATORY,  
ROYAL INSTITUTION.

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## CXI.—*Isomeric Dibenzyl Ketone Benzalanilines and Deoxybenzoin Benzalanilines. Part II.*

By FRANCIS E. FRANCIS, Ph.D., B.Sc., Lecturer in Chemistry,  
University College, Bristol.

In a previous paper (Trans., 1899, 75, 865), three isomeric additive products of benzalaniline and each of the two ketones, dibenzyl ketone

and deoxybenzoin, were described, and it was suggested that they were the analogues of the substances obtained by Schiff from ethyl acetoacetate and considered by him to be derived from the ketonic, enolic, and keto-enolic modifications of that ester. For the sake of convenience, these additive products are termed in this paper  $\alpha$ -,  $\beta$ -,  $\gamma$ -, that obtained from the pure ketone being the  $\alpha$ -, that obtained by the action of piperidine the  $\beta$ -, and that by the action of sodium ethoxide the  $\gamma$ -modification. The fact that they are slightly basic has made it possible to effect the isolation of unstable hydrochlorides which are different in the case of the  $\alpha$ - and  $\beta$ -, but identical in the case of the  $\beta$ - and  $\gamma$ -modifications. It was previously pointed out that these isomeric derivatives resemble one another very closely in appearance and properties, and that the differences in melting point alone differentiated them from each other, consequently the isolation of different hydrochlorides is important. The behaviour of these hydrochlorides with absolute alcohol is interesting; the  $\alpha$ -salt dissociates, yielding a mixture of  $\alpha$ - and  $\gamma$ -base, whereas the  $\beta$ - or  $\gamma$ -salt is transformed almost completely into the  $\alpha$ -base. The additive products from dibenzyl ketone have been more thoroughly examined than those from deoxybenzoin, and it appears that the  $\alpha$ -form is the most stable, the others being converted into it by the action of heat. It was further noticed that whereas piperidine readily converts the  $\alpha$ -, and less readily the  $\gamma$ -, into the  $\beta$ -form, phenylhydrazine, which appears to act in a similar way, converts the  $\alpha$ - into the  $\beta$ -, but not the  $\gamma$ - into the  $\beta$ -modification. It should be remarked, however, that in all these cases of transformation, the only criterion of the change is the alteration in melting point, and although so far as the work has gone at present these changes appear to be similar in the analogous substances employed, yet further investigations, which are in progress, are necessary before the question can be considered definitely settled and theoretical deductions drawn.

#### *Benzalaniline and Dibenzyl Ketone.*

(i)  *$\alpha$ -Dibenzyl Ketone Benzalaniline.*—This substance, prepared as previously described, and melting at 164–165°, showed a slight rise in the melting point on repeated recrystallisation from boiling ethyl or methyl alcohol, in which it is only slightly soluble, the maximum rise being from 165° to 168°. If heated in a sealed tube at 150°, complete decomposition into aniline, benzaldehyde, and dibenzyl ketone takes place. When melted, allowed to cool, and then recrystallised from benzene, it showed an unchanged melting point.

*$\alpha$ -Hydrochloride,  $C_{23}H_{25}ON, HCl$ .*—If the  $\alpha$ -additive product is dissolved in excess of toluene and dry hydrochloric acid gas is passed in,



the salt crystallises out in quantitative amount. On analysis, the following result was obtained :

HCl found 8·37, calculated 8·53 per cent.

It is a white, crystalline powder melting at 155·5°, and dissociating with water, giving the  $\alpha$ -base melting at 164·5°. If treated with absolute alcohol, dissociation takes place in the cold, but if the solution is heated, the base which has separated out in the form of a white, bulky, crystalline mass gradually passes into solution, complete decomposition having taken place. The base recovered after the treatment with cold alcohol has a much higher melting point, namely, 174°, and on recrystallisation from benzene was found to melt fairly constantly at 172—173·5°. The following combustion showed that it had the same composition as the  $\alpha$ -modification melting at 164—165°.

Found C=85·90 ; H=6·68.

$C_{23}H_{25}ON$  requires C=85·93 ; H=6·39 per cent.

When this substance is treated with piperidine, the melting point rises from 172—174° to 183—183·5°. The product may be recrystallised from chloroform and light petroleum, and shows an unchanged melting point, but after a few recrystallisations from pure benzene the melting point falls to 178°. It gives a hydrochloride, when treated as previously described, which melts at 158·5°. When this is treated with absolute alcohol, the resulting base melts indefinitely between 174° and 176°. Its behaviour is very similar to that of a mixture of equal amounts of the  $\alpha$ - and  $\gamma$ -modifications, as is shown in the following table :

Mixture of equal weights of $\alpha$ - and $\gamma$ -base crystallised from benzene and light petroleum.	Base from $\alpha$ -hydrochloride with absolute alcohol.
M. p. 173—174·5°.	M. p. 172—174°.
Hydrochloride: m. p. 158·5—159°.	Hydrochloride: m. p. 158·5°.
Piperidine gives base m. p. 183°, which falls to 175—176·5° on recrystallisation.	Piperidine gives base m. p. 183—183·5°, which falls to 178° on recrystallisation.
Kept at temp. of m. p. for several minutes and recrystallised, m. p. 166—168·5°.	Kept at temp. of m. p. for several minutes and recrystallised, m. p. 166—168°.

(ii)  *$\beta$ -Dibenzyl Ketone Benzalaniline*.—This modification is obtained by the action of piperidine on the  $\alpha$ -form as previously described, and

melts at 174—175°, but if kept for several minutes at a temperature of 163—164°, it slowly melts; also if melted in a tube and then recrystallised from boiling benzene, it melts at 163—164°. The change from the  $\alpha$ - to the  $\beta$ -form may also be brought about by means of phenylhydrazine either alone or dissolved in benzene; the resulting substance melts at 174°, and since no change takes place on treating this with piperidine, this modification and that obtained by using piperidine are presumably alike.

*$\beta$ -Hydrochloride.*—This salt is prepared in a similar way to the  $\alpha$ -compound. A determination of the hydrogen chloride gave the following result:

HCl found 8.17; calculated 8.53 per cent.

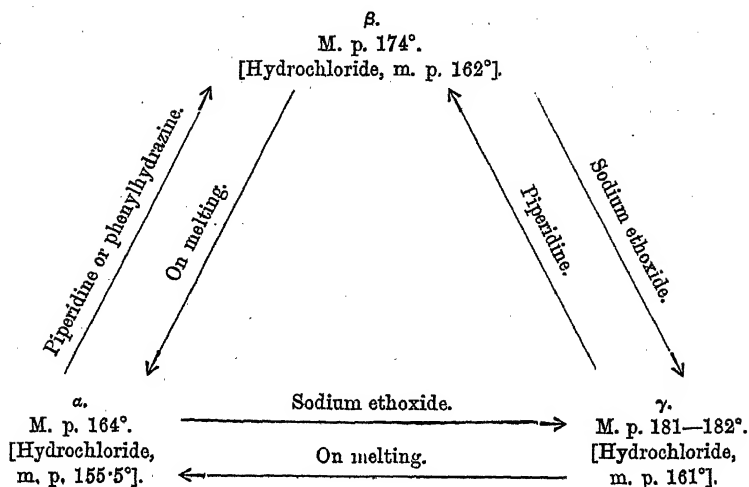
It is a white, crystalline powder melting at 162°, and is dissociated by water, giving the  $\beta$ -base melting at 174°. On treatment with absolute alcohol, dissociation also takes place; the resulting base melts at 171—172°, but on several recrystallisations this drops to 163—164°, and the product presumably is the  $\alpha$ -modification, since on treatment with piperidine the melting point rises to 174°. If the hydrochloride is kept for a few minutes at a temperature of 155°, or the temperature at which the  $\alpha$ -salt melts, it also slowly melts.

(iii)  *$\gamma$ -Dibenzyl Ketone Benzalaniline* was obtained from either the  $\alpha$ - or  $\beta$ -modification by the action of a trace of sodium ethoxide. It melted at 181—182°, but when kept at the melting point for several minutes and then recrystallised from benzene, it shows a melting point of 164°, being changed to the  $\alpha$ -modification. Piperidine with some difficulty, but not phenylhydrazine, gives the  $\beta$ -form melting at 174°.

*$\gamma$ -Hydrochloride.*—The hydrochloride (HCl = 8.46 per cent.), obtained in a similar manner to the others, appears to be the same as that from the  $\beta$ -modification. This is shown in the following table:

$\beta$ -Hydrochloride.	Hydrochloride from $\gamma$ -modification.
M. p. 161—162°.	M. p. 161°.
Dissociates with water giving base m. p. 174°.	Dissociates with water giving base m. p. 174—174.5°.
Dissociates with absolute alcohol giving base m. p. 163—164°.	Dissociates with absolute alcohol giving base m. p. 164—165°.

The following diagram illustrates the relationship between the  $\alpha$ ,  $\beta$ , and  $\gamma$ -modifications:



*Benzalaniline and Deoxybenzoin.*

(i)  *$\alpha$ -Deoxybenzoin Benzalaniline.*—As previously noticed, in the formation of the  $\alpha$ -modification melting at 154° small quantities of a substance possessing a much higher melting point are formed, but sufficient quantities of this for a satisfactory analysis have not been obtained. If, instead of keeping molecular quantities of the two constituents at a temperature of 60—70° until the additive product separates out, a solvent such as light petroleum, or ethyl or amyl alcohol be employed, insoluble substances of very high melting point are produced; these have not yet been investigated.

*$\alpha$ -Hydrochloride.*—The additive products do not appear to be so basic as those previously described, and seem capable of forming salts containing varying amounts of hydrogen chloride. If benzene is used as solvent and gaseous hydrogen chloride is passed in, small, colourless needles melting at 104° separate out. These may be recrystallised from benzene and light petroleum, and show an unchanged melting point. Two analyses gave the following results:

HCl found 6·68 and 6·70 per cent.

$C_{27}H_{28}ON$ , HCl requires HCl = 8·82 per cent.

$4C_{27}H_{28}ON, 3HCl$  „ HCl = 6·77 „

If this salt is dissolved in chloroform and the solution saturated with hydrogen chloride, on the addition of light petroleum small quantities of large, well-formed, colourless rhombohedra melting at 124° slowly separate. Even these only contain HCl = 7·10 per cent.

and rapidly dissociate on exposure to air. The first salt is much the easier to obtain. When seen in bulk, it is a white, crystalline powder which dissociates with water, giving the  $\alpha$ -base melting at 154—155°. In an analogous manner to the corresponding  $\alpha$ -salt of dibenzyl ketone benzalaniline, it also dissociates with alcohol, the melting point of the resulting base being 158·5—159°, whereas the  $\alpha$ -modification melts at 154—155°.

(ii)  *$\beta$ -Deoxybenzoin Benzalaniline*.—This modification, prepared as previously described, and melting at 164—165°, is transformed into the  $\alpha$ -form by the action of heat in a corresponding manner to the dibenzyl ketone derivative. The hydrochloride, obtained in a similar manner to the  $\alpha$ -salt, melts at 122·5°, and is dissociated with water, regenerating the  $\beta$ -base melting at 163—164°. A determination of the amount of hydrogen chloride present gave the following result:

HCl found 6·68 per cent.

$4C_{27}H_{23}ON, 3HCl$  requires HCl = 6·77 per cent.

(iii)  *$\gamma$ -Deoxybenzoin Benzalaniline*.—This modification, melting between 173° and 174°, like the corresponding dibenzyl ketone derivative, gives a hydrochloride which appears to be identical with that obtained from the  $\beta$ -form. It melts at 123°, whereas the  $\beta$ -salt melts at 122·5°, and on treatment with water gives the  $\beta$ -base melting at 164·5°.

Further experiments are being carried out with these derivatives of deoxybenzoin, and with dibenzyl ketone, using benzal-*p*-toluidine instead of benzalaniline; it has been noticed that benzal-*o*-toluidine, under precisely similar conditions, does not form additive products.

## CXII.—*Condensation of Methyl Acetonedicarboxylate.* *Constitution of Orcinoltricarboxylic Esters.*

By F. W. DOOTSON, M.A.

MANY years ago, it was shown by Cornelius and Pechmann that ethyl acetonedicarboxylate, when heated in the presence of sodium, condenses to triethyl orcinoltricarboxylate (*Ber.*, 1886, 19, 1446). More recently, the subject has been investigated by Pechmann and Wolman (*Ber.*, 1898, 31, 2014) and by Jerdan (*Trans.*, 1897, 71, 1106; 1899, 73, 808), and a variety of methods have been described for the preparation of the triethyl ester. The most successful of these methods depends upon the so-called catalytic action of sodium ethoxide, and by

means of this reagent, a maximum yield of 50 per cent. of the theoretical is obtained.

During the progress of an attempt to prepare pure methyl acetonedicarboxylate by fractional distillation of the crude material under reduced pressure, it was noticed that but a small amount of volatile material was obtained, and that a large quantity of crystalline residue remained in the retort. This residue showed little trace of the presence of carbonaceous decomposition products, was light brown in colour, and on examination proved to be trimethyl orcinoltricarboxylate.

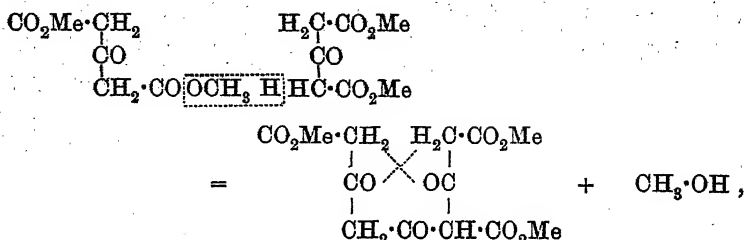
The crude methyl acetonedicarboxylate employed was prepared by the action of hydrogen chloride on a solution of dry acetonedicarboxylic acid in methyl alcohol in the usual way, and since it has been shown by Wolman and Pechmann (*loc. cit.*) that the parallel condensation is effected by allowing an alcoholic solution of ethyl acetonedicarboxylate saturated with hydrogen chloride to stand for two or three weeks, it was thought possible that the condensation had been brought about in a similar way during the process of preparation, since the methyl alcoholic solution, saturated with hydrogen chloride, had been allowed to stand for several hours before extraction with ether.

That the trimethyl orcinoltricarboxylate was not formed in this way, and was not present previous to the distillation, at all events in more than mere traces, was shown by adding the crude methyl acetonedicarboxylate to a slight excess of potassium hydroxide dissolved in alcohol, filtering off the precipitated dipotassium salt of methyl acetonedicarboxylate, and acidifying the alkaline filtrate with dilute hydrochloric acid. Trimethyl orcinoltricarboxylate, which is readily soluble in dilute potassium hydroxide solution, reprecipitated by dilute mineral acids and very sparingly soluble in dilute alcohol would, if present, have been precipitated. No such precipitate, however, was obtained, and further, a specimen of methyl acetonedicarboxylate, purified by conversion into the dipotassium salt, washing repeatedly with alcohol, acidifying with sulphuric acid, and extracting with ether in the manner described for the purification of the ethyl ester by Dunschman and Pechmann (*Annalen*, 1891, 261, 177) gave, on distillation, results precisely similar to those obtained from the crude material. The experimental details of the method are given below, but it may be here stated that the yield reaches upwards of 60 per cent. of the theoretical.

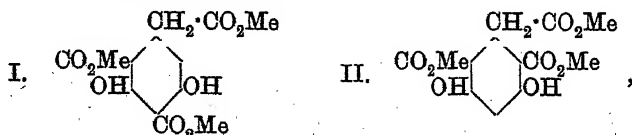
This reaction of methyl acetonedicarboxylate is of interest as marking a notable difference in behaviour between the methyl and ethyl esters. No trace of ethyl orcinoltricarboxylate could be obtained by the action of heat alone on ethyl acetonedicarboxylate—a result which

had also been previously arrived at by Jerdan (*loc. cit.*)—whilst the ease with which the condensation of the methyl ester is effected renders it one of the readiest conversions of a fatty compound into a member of the aromatic series that has hitherto been described.

Applying the explanation of the behaviour of the ethyl ester given by Cornelius and Pechmann (*Ber.*, 1886, 19, 1447) to the compound now under consideration, the course of the condensation would be represented thus :



the liberated methyl alcohol coming over in the first portions of the distillate. An intramolecular change simultaneously or subsequently takes place with liberation of water as indicated by the dotted lines, and a benzenoid compound is formed, which must possess one of the alternative formulæ represented by I and II :



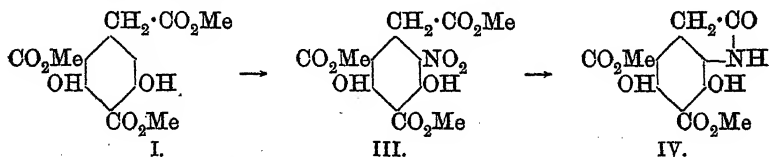
since on hydrolysis with sodium or potassium hydroxide at a moderately high temperature dihydroxyphenylacetic acid is formed, identical with that obtained by Wolman and Pechmann (*loc. cit.*) from the corresponding triethyl ester.

Although from the method of preparation it seemed highly probable that the methyl and ethyl esters are similar in constitution, this could not be regarded as certain without further evidence. This was sought by a series of experiments which at the same time confirm the view put forward by Jerdan (*loc. cit.*), that the constitution of triethyl orcinoltricarboxylate is correctly represented by formula I.

Since the only theoretical possibilities lie in the two formulæ given above, it is obvious that if the position of the remaining hydrogen atom of the benzene nucleus could be ascertained, the problem would be solved. This was done as follows.

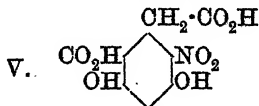
The methyl ester was treated with nitric acid in the manner described below, and the resulting nitro-compound isolated. After reduction, the nitro-derivative was reduced, but in the substance

thus obtained one mol. of alcohol had also been simultaneously eliminated. The ease with which this change takes place, occurring as it does both in alkaline solution and in suspension in dilute acids, is only consistent with the supposition that a  $\delta$ -lactam is formed, which could only happen in the case of a compound of the type of formula I. These relationships are shown thus :



Under the same conditions, triethyl orcinoltricarboxylate yields a corresponding compound, diethyl dihydroxyoxindolecarboxylate.

Like the triethyl derivative, trimethyl nitro-orcinoltricarboxylate could not be completely hydrolysed without simultaneous loss of carbon dioxide. The product obtained after boiling with sodium hydroxide was nitro-orcinoldicarboxylic acid, which, from a consideration of the work of Jordan (*Trans.*, 1899, 73, 808), would appear to have the constitution represented by the formula :



#### EXPERIMENTAL.

The condensation of trimethyl acetonedicarboxylate to trimethyl orcinoltricarboxylate was carried out as follows. Sixty-five grams of the crude ester were heated under atmospheric pressure in a distilling flask placed in an oil-bath at a temperature of 170—180°. The first portion of the distillate consisted for the greater part of methyl alcohol. After two hours heating, the pressure was reduced to about 50 mm., and a gentle current of air drawn through, the heating being continued until practically nothing further distilled over. This portion of the distillate was chiefly methyl acetoacetate. The contents of the flask were poured out into a dish while hot, and the solid mass which formed on cooling was broken up, drained by the aid of the pump, and washed several times with small quantities of alcohol, when it became pale yellow in colour. The filtrate, together with the alcoholic washings, was heated again in the same manner and a further crop of crystals obtained. The distillate, on again being subjected to the same treatment, also yielded a further crop, but the amount was very small. The total weight of washed crystalline

substance obtained, which was nearly pure trimethyl orcinoltricarboxylate, reached 34 grams.

Taking as a basis the statement of Jordan (Trans., 1899, 73, 808) that the product from acetonedicarboxylic acid and alcohol contains approximately 80 per cent. of the ester, this amount represents a yield of about 60 per cent. of that theoretically possible, whilst the yield of the ethyl ester appears to reach 50 per cent. as a maximum.

The crude substance was recrystallised twice from alcohol, decolorised by a little animal charcoal, and obtained in large, nearly colourless needles melting at 144—145° (uncorr.). The following numbers were obtained on analysis:

0.2732 gave 0.5239 CO<sub>2</sub> and 0.1150 H<sub>2</sub>O. C = 52.28; H = 4.67.

0.2687 „ 0.5142 CO<sub>2</sub> „ 0.1120 H<sub>2</sub>O. C = 52.36; H = 4.63.

C<sub>13</sub>H<sub>14</sub>O<sub>8</sub> requires C = 52.35; H = 4.69 per cent.

This substance is readily soluble in alcohol, benzene, or glacial acetic acid. Water dissolves it moderately on boiling. A dilute aqueous solution gives a dark brown colour with ferric chloride. It is dissolved easily by alkalis, and by alkali carbonates on warming, and from these it is reprecipitated by dilute mineral acids. It appears to be hydrolysed more readily than the corresponding ethyl ester. On boiling for half an hour with dilute aqueous sodium hydroxide (1 in 10), acidifying with dilute sulphuric acid, and extracting with ether, a thick, strongly acid oil was obtained, which crystallised on standing. From its general behaviour, this was presumably the dihydroxyphenylacetic acid obtained by Cornelius and Pechmann (*Ber.*, 1886, 19, 1449). It was converted into the lead salt, which after purification from water gave the following numbers on analysis:

0.2910 at 110° lost 0.0193 H<sub>2</sub>O. H<sub>2</sub>O = 6.63.

0.3591 gave 0.1888 gram PbSO<sub>4</sub>. Pb = 36.00.

0.2307 „ 0.1197 gram PbSO<sub>4</sub>. Pb = 35.46.

(C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>)<sub>2</sub>Pb.2H<sub>2</sub>O requires H<sub>2</sub>O = 6.24; Pb = 36.04 per cent.

*Nitration of Orcinoltricarboxylic Esters.*—Both the methyl and ethyl esters are nitrated with the greatest ease by dissolving them in cold nitric acid of sp. gr. 1.4, gently warming for a few minutes to 50—60°, when the nitro-compound begins to separate out, and thereupon diluting largely with water. A copious precipitate is obtained, which is best purified by several recrystallisations from methylated spirit. The methyl ester thus prepared melted at 157—158° (uncorr.), and gave the following numbers on analysis:

0.2747 gave 0.4556 CO<sub>2</sub> and 0.0932 H<sub>2</sub>O. C = 45.25; H = 3.77.

0.2070 „ 12.3 c.c. nitrogen at 20° and 760 mm. N = 4.58.

C<sub>12</sub>H<sub>12</sub>O<sub>10</sub>N requires C = 45.48; H = 3.79; N = 4.08 per cent.



The ethyl ester, nitrated and purified in the same way, melts at precisely the same temperature as ethyl orcinoltricarboxylate, namely, at 98—99° (uncorr.). The following numbers were obtained on analysis :

0.2905 gave 0.5298  $\text{CO}_2$  and 0.1269  $\text{H}_2\text{O}$ . C=49.75; H=4.85.

$\text{C}_{16}\text{H}_{18}\text{O}_{10}\text{N}$  requires C=49.87; H=4.93 per cent.

Unless the treatment with nitric acid had been unduly prolonged, the yield in each case was practically quantitative.

Both these compounds exhibit the same general solubility in the usual organic solvents as the substances from which they are derived. Their alkaline solutions have an intense blood-red colour.

*Hydrolysis of Methyl Nitro-orcinoltricarboxylate.*—Like the orcinoltricarboxylic esters, this substance can only be hydrolysed with simultaneous loss of carbon dioxide. On boiling for half an hour with dilute aqueous sodium hydroxide (1 in 10), acidifying with dilute sulphuric acid, and extracting the solution with ether, a crystalline compound was obtained, which, after purifying twice from a small quantity of water, was analysed with the following result :

0.2045 gave 0.3130  $\text{CO}_2$  and 0.0530  $\text{H}_2\text{O}$ . C=41.70; H=2.88.

0.2435 „ 12 c.c. nitrogen at 15° and 740 mm.; N=5.76.

$\text{C}_9\text{H}_7\text{O}_8\text{N}$  requires C=42.07; H=2.72; N=5.45 per cent.

As mentioned in the introduction to this paper, this compound probably has the constitution represented by formula V. It is very soluble in hot water, alcohol, or glacial acetic acid; moderately so in cold water, and practically insoluble in benzene, chloroform, or light petroleum. It melts with decomposition at 197—198° (uncorr.). Its solution gives a deep red colour with ferric chloride.

*Reduction of Nitro-orcinoltricarboxylic Esters.*—The reduction may be carried out either in alkaline solution or in suspension in acids, the same products being obtained in both cases. On account of the ready solubility of the sodium salts, it is more expedient to dissolve in dilute aqueous soda, and add a slight excess of aluminium filings. The liquid should be kept moderately cool by surrounding the flask with water, and the reduction may then be left to proceed overnight. When the aluminium is all dissolved, the liquid is somewhat diluted, filtered if necessary, and acidified. A copious crop of very fine needles is obtained; these dissolve very sparingly in the ordinary organic solvents, and are purified by recrystallisation preferably from alcohol or glacial acetic acid. The methyl ester thus obtained melted with decomposition at 260—265° (uncorr.). On analysis :

- I. 0.2352 gave 0.4422  $\text{CO}_2$  and 0.0842  $\text{H}_2\text{O}$ .  $\text{C} = 51.23$ ;  $\text{H} = 3.99$ .  
 II. 0.1355 „ 0.2542  $\text{CO}_2$  „ 0.0485  $\text{H}_2\text{O}$ .  $\text{C} = 51.16$ ;  $\text{H} = 3.97$ .  
 III. 0.3070 „ 12.7 c.c. nitrogen at  $21^\circ$  and 758 mm.  $\text{N} = 4.81$ .  
 $\text{C}_{12}\text{H}_{11}\text{O}_7\text{N}$  requires  $\text{C} = 51.24$ ;  $\text{H} = 3.91$ ;  $\text{N} = 4.98$  per cent.

Specimen I was obtained by reduction with tin and hydrochloric acid; II and III by reduction with sodium hydroxide and aluminium.

The ethyl ester melted with decomposition at  $235\text{--}236^\circ$  (uncorr.), and was analysed with the following results:

- I. 0.2330 gave 0.4600  $\text{CO}_2$  and 0.1002  $\text{H}_2\text{O}$ .  $\text{C} = 53.84$ ;  $\text{H} = 4.77$ .  
 II. 0.1589 „ 0.3105  $\text{CO}_2$  „ 0.0665  $\text{H}_2\text{O}$ .  $\text{C} = 53.29$ ;  $\text{H} = 4.65$ .  
 III. 0.2583 „ 10.3 c.c. nitrogen at  $16^\circ$  and 748 mm.  $\text{N} = 4.57$ .  
 $\text{C}_{14}\text{H}_{15}\text{O}_7\text{N}$  requires  $\text{C} = 54.36$ ;  $\text{H} = 4.85$ ;  $\text{N} = 4.53$  per cent.

Specimen I was obtained by reduction with tin and hydrochloric acid; II and III by reduction with sodium hydroxide and aluminium.

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### CXIII.—*Contribution to the Chemistry of the Aromatic Metadiamines.*

By GILBERT THOMAS MORGAN, D.Sc.

THE halogen derivatives of *m*-phenylenediamine and its homologues have hitherto been prepared either by the direct action of the halogen on the base or its acyl derivative (Jackson and Calvert, *Amer. Chem. J.*, 1896, 18, 465), or by the reduction of aromatic dinitro-compounds containing chlorine or bromine (Nietzki and Rebe, *Ber.*, 1892, 25, 3005). The latter method, however, does not always lead to the formation of a substituted diamine, owing to the fact that the halogen radicles situated in the ortho- or para-positions relatively to the nitro-groups of the dinitro-compounds are readily removed by the action of the reducing agent. 1-Chloro-2:4-dinitrobenzene, when reduced with tin and hydrochloric acid, yields 1-chloro-2:4-phenylenediamine (Beilstein and Kurbatoff, *Annalen*, 1879, 197, 76), whereas the corresponding bromo-compound, under these conditions, loses its halogen radicle, and becomes converted into *m*-phenylenediamine (Zincke and Sintenis, *Ber.*, 1872, 5, 791). Similarly, Jackson and Calvert (*loc. cit.*) showed that 1:3:5-tribromo-2:4-dinitrobenzene lost all its bromine when treated with tin and hydrochloric acid, giving rise to *m*-phenylenediamine, and also that the halogen is not removed by reduction with zinc and acetic acid.

Further investigation shows, however, that 1-bromo-2:4-dinitrobenzene may be reduced, without the elimination of bromine, by the action of iron filings in the presence of a small quantity of hydrochloric acid, the method employed in the commercial preparation of the aromatic diamines.

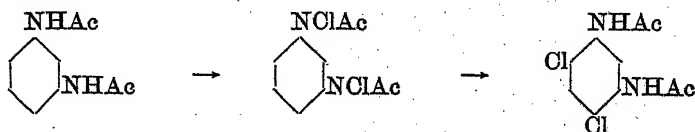
The constitution of the new base, 1-bromo-2:4-phenylenediamine, is known from its mode of formation, and also from the fact that, on treatment with nitrous acid in the presence of cuprous bromide, it yields 1:2:4-tribromobenzene; it is isomeric with the bromo-*m*-phenylenediamine (m. p. 93—94°) obtained by Jackson and Calvert on reducing 1:3:5:6-tetrabromo-2:4-dinitrobenzene with tin and hydrochloric acid, the latter diamine having, in all probability, the symmetrical formula indicated by these investigators.

1-Chloro-2:4-phenylenediamine is readily prepared by the iron and hydrochloric acid method of reduction; the corresponding iodo-base could not, however, be obtained from 1-iodo-2:4-dinitrobenzene, for, under these conditions, the iodine atom is simultaneously eliminated, and *m*-phenylenediamine results.

Diacetyl-1-chloro-2:4-phenylenediamine, when treated with chlorine in glacial acetic acid solution, yields a dichloro-derivative, which, on hydrolysis, is converted into 1:5-dichloro-2:4-phenylenediamine; this base may also be prepared by the direct chlorination of diacetyl-*m*-phenylenediamine, its constitution being determined by converting it into 1:2:4:5-tetrachlorobenzene by means of the Sandmeyer reaction.

The researches of Bender (*Ber.*, 1886, 19, 2272), Slosson (*Ber.*, 1895, 25, 3265), Chattaway and Orton (*Trans.*, 1899, 75, 1046; this vol., 134, 800), and others have shown that the acyl derivatives of the primary aromatic monamines, on treatment with hypochlorous or hypobromous acid, yield substituted nitrogen chlorides or bromides containing the halogen atom attached to nitrogen, &c., and also that these substances, by intramolecular rearrangement, give rise to the acyl derivatives of the corresponding halogen-substituted bases.

A similar reaction occurs with the diacyl derivatives of *m*-phenylenediamine, each molecule of diacetyl-*m*-phenylenediamine, for example, taking up two atoms of chlorine, and forming *m*-phenylenediacetyldichloramine; this dichloride, on digestion with warm glacial acetic acid, is readily transformed into diacetyl-1:5-dichloro-2:4-phenylenediamine, the changes involved in these operations being indicated by the following diagram:



The reaction with hypobromous acid takes a similar course, and the dibromo-*m*-phenylenediamine, produced by hydrolysing the diacyldibromo-*m*-phenylenediamine, is found to be identical with the base obtained by Jackson and Calvert by direct bromination.

The constitution of the dibromo-base is determined by means of the Sandmeyer reaction; under this treatment, it yields 1:2:4:5-tetrabromobenzene, and is therefore 1:5-dibromo-2:4-phenylenediamine; this substance may also be prepared from diacetyl-1-bromo-2:4-phenylenediamine by direct bromination and subsequent hydrolysis.

When diacetyl-2:4-tolylenediamine is treated with chlorine in glacial acetic acid, it yields a monochloro-derivative, which, on hydrolysis, gives rise to a new chloro-2:4-tolylenediamine. This base is isomeric with 2-chloro-3:5-tolylenediamine obtained by Nietzki and Rebe (*loc. cit.*), and is shown to be 5-chloro-2:4-tolylenediamine, by conversion into the corresponding trichlorotoluene, through the agency of the Sandmeyer reaction. The trichlorotoluene produced melts at 82°, and is identical with 2:4:5-trichlorotoluene, obtained by the direct chlorination of toluene (Limpricht, *Annalen*, 1866, 139, 326); the constitution of this substance was demonstrated by Seelig, who converted it successively into 2:4:5-trichloro-3:6-dinitrotoluene, 2:4:5-trichloro-3:6-tolylenediamine, and trichlorotoluquinone (*Annalen*, 1887, 237, 146).

#### EXPERIMENTAL.

##### 1-Bromo-2:4-phenylenediamine.

An excess of iron filings (70 grams) is slowly added to 40 grams of 1-bromo-2:4-dinitrobenzene suspended in 400 c.c. of hot water acidified with 5 c.c. of concentrated hydrochloric acid, the mixture being continually shaken during the operation. The dinitro-compound gradually disappears, the solution darkens, and considerable heat is developed, 400 c.c. of cold water being added during the reduction in order to moderate the action. When the odour of the nitro-compound has almost disappeared, the mixture is heated to boiling on the sand-bath, and 10 grams of sodium hydrogen carbonate are introduced; the solution is then rapidly filtered from the black precipitate of hydrated magnetic oxide and unaltered iron, the latter washed with 100 c.c. of boiling water, and the total filtrate cooled by a mixture of ice and salt. After several hours, the solution deposits brownish-grey, acicular crystals of 1-bromo-2:4-phenylenediamine, the yield being about 14–15 grams. The filtrate still contains a considerable amount of the diamine, as may be shown by the formation of a chrysoidine by the action of diazotised aniline. The dissolved base may either be extracted with chloroform or obtained as hydrochloride by evaporating the acidified solution; the latter method, however, is not to be

recommended, as a portion of the substance is destroyed by atmospheric oxidation. A larger yield of the crystalline precipitate cannot be obtained by employing less water in the reduction, for, under these conditions, the reaction becomes so violent that the bromo-base is totally destroyed, and *m*-phenylenediamine and ammonia only are produced.

1-Bromo-2:4-phenylenediamine readily dissolves in hot water, but is less soluble in the cold; the base rapidly oxidises when moist, and it is therefore preferable to crystallise the compound from an anhydrous solvent. It separates from benzene in irregular clusters of colourless, acicular prisms which soon turn pink; its melting point is 111—112°. The base is readily soluble in the ordinary organic solvents, excepting light petroleum, in which it dissolves but sparingly.

0.1491 gave 0.1498 AgBr. Br = 42.75.

$C_6H_7N_2Br$  requires Br = 42.78 per cent.

*Dibenzoyl-1-bromo-2:4-phenylenediamine*, readily obtained by the Schotten-Baumann reaction, crystallises from benzene or chloroform in felted, white needles, and melts at 178.5°.

0.2100 gave 0.0964 AgBr. Br = 19.53.

0.3705 „ 24.1 c.c. moist nitrogen at 22° and 761 mm. N = 7.38.

$C_{20}H_{15}N_2Br$  requires Br = 20.25; N = 7.27 per cent.

*Diacetyl-1-bromo-2:4-phenylenediamine*, prepared by adding 1-bromo-2:4-phenylenediamine to a mixture of equal parts by weight of glacial acetic acid and acetic anhydride, crystallises from chloroform or benzene in white, felted needles and melts at 197—198°. The diamine is readily acetylated by acetic anhydride without the application of external heat; prolonged boiling of the base with the above mixture results in the formation of tarry products.

0.1145 gave 0.0819 AgBr. Br = 30.25.

$C_{10}H_{11}N_2Br$  requires Br = 29.52 per cent.

1-Bromo-2:4-phenylenediamine readily reacts with diazonium salts; with benzenediazonium chloride, it yields bromochrysoidine hydrochloride, a substance crystallising from dilute hydrochloric acid in greenish-black, anthracitic needles. Potassium bromochrysoidine-sulphonate, obtained by the action of diazobenzenesulphonic acid, crystallises from water in yellowish-brown leaflets with a bronzy reflex.

A solution of 6 grams of 1-bromo-2:4-phenylenediamine and 5 grams of cuprous bromide in 40 c.c. of concentrated hydrobromic acid and 20 c.c. of water, when treated at 90° with a 20 per cent. solution of sodium nitrite (2 mols.) and subsequently distilled in steam, yields a distillate containing 1:2:4-tribromobenzene; this substance, after

two crystallisations from alcohol, melts at 42—43°, the melting point of the pure tribromo-compound being 44°.

1-Chloro-2:4-phenylenediamine is readily prepared from the corresponding dinitro-compound by the method of reduction described above. The solution produced by reducing the 1-chloro-2:4-dinitrobenzene, derived from 100 grams of chlorobenzene, with 260 grams of iron filings, 30 c.c. of hydrochloric acid, and 1500 c.c. of water, yielded, after neutralisation with 35 grams of sodium hydrogen carbonate, 80 grams of crystallised base, whilst a further yield of 20 grams was obtained from the filtrates by extraction with chloroform.

*Dibenzoyl-1-chloro-2:4-phenylenediamine*, produced from the chloro-base by the Schotten-Baumann reaction, crystallises from chloroform or benzene in white, felted needles melting at 178°.

0.1800 gave 0.0750 AgCl. Cl = 10.31.

$C_{20}H_{15}N_2Cl$  requires Cl = 10.12 per cent.

*Chlorochrysoidine hydrochloride*, prepared by adding a solution of benzenediazonium chloride to a dilute hydrochloric acid solution of 1-chloro-2:4-phenylenediamine, crystallises from water in long, fusiform clusters of greenish-black, anthracitic needles.

The base  $C_6H_5N_2 \cdot C_6H_2Cl(NH_2)_2$  crystallises from benzene in orange leaflets melting at 149°.

0.1489 gave 0.0860 AgCl. Cl = 14.12.

0.2253 „ 46.1 c.c. moist nitrogen at 20° and 766 mm. N = 22.57.

$C_{12}H_{11}N_4Cl$  requires Cl = 14.40; N = 22.81 per cent.

When dyed on cotton mordanted with tannin, it gives a somewhat redder shade of orange than ordinary chrysoidine. Potassium chlorochrysoidinesulphonate, obtained by the action of diazobenzene-sulphonic acid on 1-chloro-2:4-phenylenediamine, crystallises from water in orange-brown leaflets having a bronzy reflex.

#### 1:5-Dichloro-2:4-phenylenediamine.

Diacetyl-1-chloro-2:4-phenylenediamine, prepared by adding 28 grams of powdered 1-chloro-1:2-phenylenediamine to a mixture of 15 grams of glacial acetic acid and 50 grams of acetic anhydride, separates from the solution on cooling and, after recrystallisation from water, melts at 242—243°. A current of chlorine passed into a solution of this diacetyl derivative in 2—3 parts of glacial acetic acid produces a precipitate of diacetyl-1:5-dichloro-2:4-phenylenediamine, this substance being almost insoluble in the solvent. When recrystallised from benzene, diacetyl-1:5-dichloro-2:4-phenylenediamine melts at 260°. 1:5-Dichloro-2:4-phenylenediamine,  $C_6H_2Cl_2(NH_2)_2$ , is prepared from a solution of its diacetyl derivative in excess of

sodium hydroxide on prolonged boiling; the hydrolysis may also be effected by the action of hot alcoholic hydrochloric acid. The base crystallises from dilute alcohol in colourless needles, and from benzene in feathery aggregates of acicular prisms; it darkens slightly on exposure and melts at 136—137°.

0.1167 gave 0.1882 AgCl. Cl = 40.75.

0.1092 „ 15.6 c.c. moist nitrogen at 22° and 759 mm. N = 16.16.

$C_6H_6N_2Cl_2$  requires Cl = 41.13; N = 15.82 per cent.

Diacetyl-1:5-dichloro-2:4-phenylenediamine may also be prepared by the direct chlorination of diacetyl-*m*-phenylenediamine, the latter substance, when dissolved in 3—4 parts by weight of glacial acetic acid and treated with excess of chlorine (over 2 mols.), yields the dichloro-derivative exclusively; there is apparently no tendency for the formation of a trichloro-compound.

Three grams of the dichloro-base and 3.2 grams of cuprous chloride are dissolved in 35 c.c. of concentrated hydrochloric acid and 10 c.c. of water and treated at 80—90° with 1.6 grams of sodium nitrite dissolved in 16 c.c. of water; the solution is then heated to boiling for a short time, and subsequently distilled in steam. The solid, yellow product obtained in the 'distillate has an odour of chloranil, and on crystallisation from alcohol yields 1:2:4:5-tetrachlorobenzene; this compound, when purified by sublimation, is obtained in long, colourless needles melting at 137—138°.

*Action of Hypochlorous Acid on Diacetyl-m-phenylenediamine.*

Ten grams of diacetyl-*m*-phenylenediamine are dissolved in 400 c.c. of boiling water, and the solution rapidly cooled to obtain small crystals; 30—40 grams of potassium hydrogen carbonate are then added, and the mixture treated with 150 c.c. of a sodium hypochlorite solution containing 30 grams of chlorine per litre. After a short time the precipitate is collected, washed until free from hypochlorite, and dried on porous plates. The product, *m*-phenylenediacetyldichloramine,  $C_6H_4(NCl \cdot CO \cdot CH_3)_2$ , is readily soluble in benzene or chloroform, and crystallises from its solution, on the addition of light petroleum, in hard, colourless prisms or octahedra. The compound liberates iodine from a solution of potassium iodide, and a quantitative examination showed that it contains 2 atoms of labile chlorine. Weighed portions were dissolved in chloroform, treated with excess of potassium iodide solution, and titrated with standard thiosulphate.

0.1718 liberated 0.3358 I. Cl = 27.42.

0.2110 „ 0.4129 I. Cl = 27.45.

$C_{10}H_{10}O_2N_2Cl_2$  requires Cl = 27.20 per cent.

*m*-Phenylenediacetyldichloramine melts at 150—151° to a colourless liquid, which almost immediately decomposes with explosive violence; when boiled with glacial acetic acid, it is converted into diacetyl-1:5-dichloro-2:4-phenylenediamine, the latter compound crystallising from the solvent in white, felted needles. The diamine produced through the agency of hypochlorous acid was shown to be identical with that obtained by chlorination by the direct comparison of the two specimens and their benzoyl derivatives; moreover, it yields 1:2:4:5-tetrachlorobenzene when submitted to the Sandmeyer reaction. *Dibenzoyl-1:5-dichloro-2:4-phenylenediamine*, prepared as a means of identifying the dichloro-base, crystallises from benzene or chloroform in white, felted needles which darken on exposure to light, and melt at 187°.

0.1128 gave 0.083 AgCl. Cl = 18.20.

$C_{20}H_{14}N_2Cl_2$  requires Cl = 18.44 per cent.

When finely divided dibenzoyl-*m*-phenylenediamine is suspended in a saturated solution of potassium hydrogen carbonate and treated with excess of sodium hypochlorite, it yields a dichloramine corresponding with *m*-phenylenediacetyldichloramine; it is, however, less stable than this compound, and readily passes into dibenzoyl-1:5-dichloro-2:4-phenylenediamine (m. p. 187°) on boiling with chloroform or benzene.

*Bromination of Diacetyl-1-bromo-2:4-phenylenediamine.*

Ten grams of diacetyl-1-bromo-2:4-phenylenediamine, dissolved in two parts by weight of glacial acetic acid, are treated with 1 mol. of bromine diluted with two parts by weight of the same solvent; the product, added to water containing a little sulphurous acid, yields a brown precipitate which is hydrolysed with 30 c.c. of concentrated hydrochloric acid. The base, obtained on neutralising the acid solution, crystallises from alcohol in needles and melts at 135°; it appears to be identical with the dibromo-2:4-phenylenediamine prepared by Jackson and Calvert by the direct bromination of diacetyl-*m*-phenylenediamine (*Amer. Chem. J.*, 1896, 18, 482). This diamine, when submitted to the Sandmeyer reaction in the presence of cuprous bromide, yields a tetrabromobenzene, which, after sublimation and recrystallisation from alcohol, melts at 174° and does not depress the melting point of the 1:2:4:5-tetrabromobenzene prepared by the direct bromination of *p*-dibromobenzene; accordingly, the base is 1:5-dibromo-2:4-phenylenediamine.



*Action of Hypobromous Acid on Diacetyl-m-phenylenediamine.*

The finely divided diacetyl-*m*-phenylenediamine is suspended in a cold, saturated solution of potassium hydrogen carbonate and treated with excess of potassium hypobromite solution; the insoluble product has a yellow colour when first collected, but becomes almost colourless on drying. This substance still gives the substituted bromamine reaction with potassium iodide, but seems to consist principally of the transformed diacetyldibromo-*m*-phenylenediamine. A portion crystallised from chloroform melts at 259—260°, this being the melting point of diacetyl-1:5-dibromo-2:4-phenylenediamine; the melting point of the diamine, obtained on hydrolysis, is 133°, whilst that of pure 1:5-dibromo-2:4-phenylenediamine is 135°.

*5-Chloro-2:4-tolylenediamine.*

A solution of diacetyl-2:4-tolylenediamine (m. p. 221°) in 3½ parts by weight of glacial acetic acid, when treated with 1 mol. of chlorine and subsequently diluted with water, yields a brownish-white, crystalline precipitate of diacetyl-5-chloro-2:4-tolylenediamine. The corresponding diamine, obtained by hydrolysing the preceding compound with alcoholic hydrochloric acid and neutralising the hydrochloride solution with ammonia, crystallises from water in colourless, nacreous leaflets which turn pink on exposure to the air. When crystallised from benzene, the base separates either in long, colourless, elastic lamellæ or in thin, rectangular plates; it melts at 120—121°.

0.1328 gave 0.1226 AgCl. Cl = 22.82.

0.2185 „ 34.2 c.c. moist nitrogen at 18° and 758 mm. N = 18.03.

C<sub>7</sub>H<sub>9</sub>N<sub>2</sub>Cl requires Cl = 22.68; N = 17.89 per cent.

The *diacetyl* derivative crystallises in small, acicular prisms melting at 239—240°.

Three grams of sodium nitrite, dissolved in 30 c.c. of water, are slowly added to a hot solution of 4 grams of 5-chloro-2:4-tolylenediamine and 4 grams of cuprous chloride in 30 c.c. of concentrated hydrochloric acid and 10 c.c. of water; the mixture is maintained at 80—90° until the evolution of nitrogen has ceased, and subsequently distilled in steam. The volatile product, consisting of 1.5 grams of crude trichlorotoluene, is purified by sublimation and recrystallisation from alcohol; it crystallises in colourless, flattened needles and melts at 81.5°, the melting point of Limpricht's 2:4:5-trichlorotoluene being 82°.

1:5-Dichloro-2:4-phenylenediamine, its bromine analogue, and

5-chloro-2:4-tolylenediamine all contain substituent radicles in both the para-ortho-positions relatively to the amino-groups, and they react less readily with diazonium salts than the mono-substituted *m*-phenylenediamines; they do, however, combine with certain diazo-compounds such as diazobenzenesulphonic acid, and hence the azo-residue must enter the ortho-position contiguous to the two amino-radicles. A study of these azo-compounds will form the subject of a subsequent communication.

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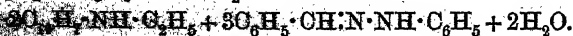
#### CXIV.—*Action of Aromatic Aldehydes on Derivatives of β-Naphthylamine.*

By GILBERT THOMAS MORGAN, D.Sc.

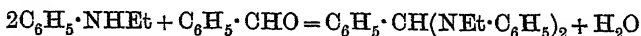
BENZYLIDENE-β-NAPHTHYLAMINE is the first product of the action of benzaldehyde on β-naphthylamine, and on further condensation with excess of the base it yields a colourless substance (dihydrophenyl-naphthacridine?), from which phenylnaphthacridine is obtained by oxidation (Claisen, *Annalen*, 1889, 239, 272).

The formation of condensation products containing the aldehydic carbon atom directly attached to the aromatic nucleus of the β-naphthylamine residue takes place, however, far less readily with benzaldehyde than with formaldehyde, for in the case of the latter the methylene residue always takes up its position in the ring unless the amine employed already contains a substituent radicle in the α-position contiguous to the β-amino-group (Morgan, *Trans.*, 1898, 73, 536; this vol., 814).

When ethyl-β-naphthylamine is treated with benzaldehyde dissolved in cold glacial acetic acid, a substance is slowly produced by the elimination of one mol. of water from three mols. of the aldehyde and two of the base.  $3\text{C}_6\text{H}_5 \cdot \text{CHO} + 2\text{C}_{10}\text{H}_7 \cdot \text{NH} \cdot \text{C}_2\text{H}_5 = \text{C}_{45}\text{H}_{42}\text{O}_2\text{N}_2 + \text{H}_2\text{O}$ . This compound, a well defined crystalline substance melting at 148°, is readily hydrolysed into its generators by mineral acids, and therefore does not contain an aldehydic carbon atom attached to the naphthalene nuclei. When treated with phenylhydrazine in warm glacial acetic acid, it is decomposed with the formation of benzylidenephénylhydrazones and the regeneration of ethyl-β-naphthylamine.

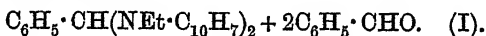


Although the study of the anhydro-bases derived from the aromatic aldehydes and primary aromatic amines has engaged the attention of many investigators, yet very few instances of the combination of benzaldehyde and its homologues with monoalkyl aromatic amines have hitherto been recorded. By the action of this aldehyde on ethylaniline, Schiff obtained the base benzylidenediethyldiphenylamine as an uncrystallisable resin, the condensation taking place in the following manner:

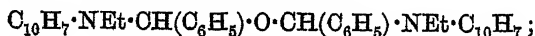


(*Annalen, Suppl.*, 1864, 3, 363).

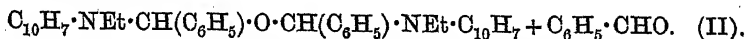
If the initial phase of the reaction with ethyl- $\beta$ -naphthylamine takes a similar course, the crystalline product may result from the combination of the analogous anhydro-base,  $C_6H_5 \cdot CH(NEt \cdot C_{10}H_7)_2$ , with 2 mols. of benzaldehyde, its constitution, on this assumption, being represented by the molecular formula



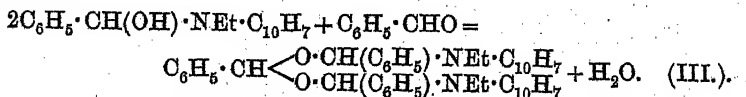
On the other hand, the initial product of the reaction may be the additive compound  $C_6H_5 \cdot CH(OH) \cdot NEt \cdot C_{10}H_7$ , and the elimination of water may be regarded as taking place between two mols. of the substance with the formation of the anhydride



the final product would then result from the combination of the latter with 1 mol. of benzaldehyde, the hypothetical formula corresponding with this view being



Lastly, the condensation may be supposed to take place in such a manner that the third molecule of benzaldehyde also undergoes rearrangement, the reaction being represented by the following equation:



On this hypothesis, the substance is represented by a constitutional formula in which the three benzylidene residues are represented as forming an essential part of the structure of the molecule.

If the compound contains benzaldehyde of crystallisation, it might be expected to crystallise from different solvents with varying amounts of this substance; however, it separates unchanged from its solutions in benzene, acetone, ethyl acetate, acetic acid, chloroform, and the alcohols. It is quite stable at its melting point, and does not give off

benzaldehyde when heated at temperatures above the boiling point of this liquid. Moreover, its decomposition by phenylhydrazine indicates that the three benzylidene residues are eliminated simultaneously. The evidence obtained from the general behaviour of the substance is, therefore, in favour of the constitution indicated by formula III.

On the other hand, determinations of the molecular weight in benzene—a solvent which favours association—indicate that the molecular complexity of the dissolved substance is less than that represented by the formula  $C_{45}H_{42}O_2N_2$ . The molecular weight of the undissociated compound should be 642, whereas the experimental values are approximately only half this, thus indicating a dissociation into two molecules.

This may be taken as evidence in favour of formula II, but it is well known that many substances, whose chemical reactions indicate a high molecular complexity, give, under these conditions, molecular weights corresponding with simpler molecules. This is the general behaviour of racemic compounds, and similar discrepancies, attending the determinations of molecular weights in benzene solutions, have been noticed in the case of naphthalene picrate (Anschütz, *Annalen*, 1889, 253, 343), and also in that of the mixed alkyl diazoamides (Meldola, *Trans.*, 1890, 57, 806).

It was not found possible by further condensation with excess of ethyl- $\beta$ -naphthylamine in the presence of zinc chloride, to convert the compound  $C_{45}H_{42}O_2N_2$  into a phenyldinaphthylmethane derivative containing the benzylidene residue directly attached to the naphthalene nuclei, and similar attempts to condense the dialkyl- $\beta$ -naphthylamines with benzaldehyde also proved unsuccessful.

The halogen derivatives of  $\beta$ -naphthylamine yielded, with formaldehyde, colourless bases of the type  $CH_2(NHX)_2$  (Morgan, this vol., *loc. cit.*); with benzaldehyde, and its analogues, they gave coloured compounds of the type  $Ph\cdot CH\cdot NX$ .

All anhydro-bases containing the group  $-CH\cdot N-$  attached to two aromatic nuclei are more or less coloured; the analogy between these bases and the azo-compounds has been referred to by Weil (*Ber.*, 1894, 27, 3317), and more recently by Möhlau (*Ber.*, 1898, 31, 2250), who suggested the name "azomethine" for the above group in order to recall its relationship to the azo-radicle  $-N\cdot N-$ .

The development of colour produced by the introduction into a molecule of an azomethine group is, however, invariably less than that which results from the presence of an azo-radicle, and, moreover, the effect is greatly modified by the nature and position of the substituent radicles of the aromatic nuclei.

The introduction of hydroxyl into the para-position relatively to the azomethine carbon atom diminishes the colour of the substance, whereas

the presence of this radicle in the ortho-position greatly enhances it. The benzylidene anhydro-bases from chloro- and bromo-naphthylamines are lemon-yellow; the corresponding derivatives of *p*-hydroxybenzaldehyde, on the one hand, are almost colourless, whilst the salicylaldehyde compounds, on the other, have a decided orange colour. A reference to the literature of the anhydro-bases shows that this relationship holds generally, and the phenomenon bears a certain analogy to the well-known colour difference between the *o*- and *p*-nitrophenol. In both series of compounds, the position of the hydroxyl group relatively to the chromophore has a marked influence on the colour of the substance. The direct attachment of an aromatic nucleus to the aldehydic carbon atom is not essential for the production of a coloured azomethine derivative, inasmuch as the anhydro-bases derived from cinnamaldehyde are more strongly coloured than those obtained from benzaldehyde.

The anhydro-bases,  $R \cdot CH : NX$ , very frequently possess the property of combining additively with anhydrous hydrogen cyanide; the reaction is, however, not general, for the presence of acidic groups hinders the combination, and may even prevent it altogether (Eibner, *loc. cit.*).

The colour of azo- and azomethine-compounds depends on the integrity of the double linking in their chromophores; the former are rendered colourless by the addition of hydrogen to the azo-radicle,  $C_6H_5 \cdot N : N \cdot C_6H_5 + H_2 = C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$ ; the latter (when they contain no nitro-groups) may be decolorised by the addition of hydrogen cyanide to the azomethine group,  $C_{10}H_7Br \cdot N : CH \cdot C_6H_5 + HCN = C_{10}H_7Br \cdot NH \cdot CH(CN) \cdot C_6H_5$ .

Hydrocyanides of this type have been obtained from the anhydro-bases of benzenoid amines (von Miller and Plöchl, *Ber.*, 1892, 25, 2056; 1898, 31, 2699), and several examples, obtained from naphthalenoid amines, are described in the experimental part of this paper. In some cases, the cinnamylidene anhydro-bases, for example, the change from the coloured azomethine derivative to the colourless hydrocyanide, is very striking.

A nitro-group introduced into an azomethine compound produces far more effect in increasing the colour of the substance than any other substituent radicle; it also greatly hinders the combination of the base with hydrogen cyanide. It was not found possible to bring about combination between this reagent and the anhydro-bases derived from the chloro- and bromo- $\beta$ -naphthylamines and the nitrobenzaldehydes.

In those cases, however, where the addition of hydrogen cyanide to a nitro-anhydro-base has been effected, the hydrocyanide is found to be coloured (von Miller and Plöchl, *Ber.*, 1892, 25, 2056). The

colour of a nitro-anhydro-base is due to the presence of both azomethine and nitroxyl ( $\text{NO}_2$ ) chromophores, and although the former may be destroyed by the addition of hydrogen cyanide, the effect of the latter persists, and it is to this that the colour of the hydrocyanide is due.

### EXPERIMENTAL.

#### *Action of Benzaldehyde on Ethyl- $\beta$ -naphthylamine.*

Benzaldehyde (50 grams) is added to a solution of 50 grams of ethyl- $\beta$ -naphthylamine in 100—150 grams of glacial acetic acid, and in 24 hours rosettes of colourless, prismatic needles appear in the mixture, the precipitation being complete after 2—3 days; the yield of crude product is about 95 grams. The substance is purified by recrystallisation from ethyl acetate or alcohol; it separates from these solvents in fern-like aggregates of lustrous, colourless leaflets, and melts at  $148^\circ$ . The alcoholic solution exhibits a blue fluorescence.

0.1692 gave 0.5212  $\text{CO}_2$  and 0.1046  $\text{H}_2\text{O}$ .  $\text{C} = 84.01$ ;  $\text{H} = 6.87$ .

0.1552 „ 0.4777  $\text{CO}_2$  „ 0.0917  $\text{H}_2\text{O}$ .  $\text{C} = 84.05$ ;  $\text{H} = 6.58$ .

0.1882 „ 7.8 c.c. moist nitrogen at  $17^\circ$  and 771 mm.  $\text{N} = 4.82$ .

0.1999 „ 8.0 c.c. „ „  $17^\circ$  „ 771 mm.  $\text{N} = 4.71$ .

[ $\text{C}_{45}\text{H}_{42}\text{O}_2\text{N}_2$  requires  $\text{C} = 84.11$ ;  $\text{H} = 6.52$ ;  $\text{N} = 4.36$  per cent.]

The compound crystallises unchanged from its solutions in benzene, acetic acid, acetone, chloroform, ethyl acetate and methyl, ethyl or amyl alcohols. When heated in a sulphuric acid bath at  $189^\circ$ , a temperature  $10^\circ$  above the boiling point of benzaldehyde, it melts to a light brown liquid, but undergoes no further change; on cooling, it resolidifies into a transparent, brown cake resembling amber, and after recrystallisation from ethyl acetate melts at  $145^\circ$ , and does not depress the melting point of the pure substance.

Hot concentrated hydrochloric acid readily hydrolyses it into its generators. Weighed portions were hydrolysed in this manner, and the solutions distilled in steam to remove benzaldehyde; the liquid in the distilling flask was evaporated to dryness, and the hydrochloride weighed; the yields obtained varied from 59 to 60 per cent., the theoretical value being 63 per cent. The low result is probably due to the appreciable volatility of ethyl- $\beta$ -naphthylamine hydrochloride at the temperature of the water-bath. The regenerated base was shown to be ethyl- $\beta$ -naphthylamine by taking the melting point of its hydrochloride ( $234^\circ$ ), and also by converting it into its characteristic azo-derivative with *p*-nitrobenzenediazonium chloride. *p*-Nitrobenzene-*azethyl- $\beta$ -naphthylamine*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_8\cdot\text{NH}\text{Et}$ , prepared by adding a glacial acetic acid solution of ethyl- $\beta$ -naphthylamine to an aqueous solution of diazotised *p*-nitraniline containing excess of sodium

acetate, crystallises from alcohol or ethyl acetate in lustrous, green needles having a bronzy reflex, and melts at 162—163°.

0.1414 gave 21.2 c.c. moist nitrogen at 18° and 761 mm.  $N = 17.34$ .

$C_{18}H_{16}O_2N_4$  requires  $N = 17.50$  per cent.

About half a gram of the compound  $C_{45}H_{42}O_2N_2$ , dissolved in a 20 per cent. solution of phenylhydrazine in 6 c.c. of glacial acetic acid, was gently heated for a few minutes until the solution became brownish-yellow; the liquid was then cooled in ice, and 4 c.c. of water added to complete the precipitation of the benzyldenenphenylhydrazone. The precipitate, collected on a Gooch crucible, was washed with dilute acetic acid and water, dried at 110—120°, and weighed. The melting point of the hydrazone prepared in this manner is 151°, whereas that of the pure substance is 152.5°.

0.2972 yielded 0.2681 benzyldenenphenylhydrazone.

$3C_6H_5 \cdot CH$  found = 41.4. Calculated = 42.0 per cent.

Determinations of the molecular weight of the condensation product by the cryoscopic method in benzene solution gave the following results:

0.4524	dissolved in 20.80 benzene	gave $\Delta t$ 0.327°.	$M = 326$ .
0.5156	„ 20.71 „ „	0.372.	$M = 328$ .
0.8446	„ 20.71 „ „	0.604.	$M = 331$ .
0.4512	„ 20.03 „ „	0.347.	$M = 318$ .
1.0820	„ 20.03 „ „	0.797.	$M = 332$ .
1.2964	„ 20.03 „ „	0.947.	$M = 335$ .

The calculated values for no dissociation and for dissociation into 2 mols. are 642 and 321 respectively.

The compound  $C_{45}H_{42}O_2N_2$  is not converted into a phenyldinaphthylmethane base by heating with excess of ethyl- $\beta$ -naphthylamine and zinc chloride at temperatures varying from 100° to 130°. Similar attempts to bring about condensation between dimethyl- $\beta$ -naphthylamine and benzaldehyde also proved unsuccessful.

*Anhydro-bases from 1-Bromo-2-naphthylamine and 1-Chloro-2-naphthylamine and their Hydrocyanides.*

When benzaldehyde is added to a glacial acetic acid solution of 1-bromo-2-naphthylamine or its chlorine analogue, the mixture assumes an orange-yellow colour, and when stirred for a short time deposits a yellow, crystalline precipitate of the anhydro-base; this method is generally applicable to the preparation of the anhydro-bases from aromatic amines and aldehydes.

The hydrogen cyanide employed in forming the addition compounds

was obtained by the action of 50 per cent. sulphuric acid on pure potassium cyanide and freed from moisture and traces of mineral acids by rectification from calcium chloride and potassium cyanide.

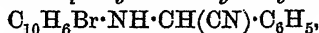
The recrystallised anhydro-base, placed in a large weighing bottle, was cooled in ice and treated with excess of hydrogen cyanide, the mixture being shaken at intervals for one or two days.

*Benzylidene-1-bromo-2-naphthylamine*,  $C_{10}H_6Br \cdot N:CH \cdot C_6H_5$ , crystallises from light petroleum in lemon-yellow prisms and melts at 93—94°.

0.1200 gave 0.0715 AgBr. Br = 25.35.

$C_{17}H_{12}NBr$  requires Br = 25.80 per cent.

*Benzylidene-1-bromo-2-naphthylamine hydrocyanide*,



crystallises from methyl alcohol or benzene and light petroleum in transparent, colourless leaflets melting at 92°; it is almost insoluble in hydrogen cyanide, and turns yellow on exposure to the atmosphere.

0.2059 gave 15.3 c.c. moist nitrogen at 15° and 744 mm. N = 8.51.

$C_{18}H_{13}N_2Br$  requires N = 8.31 per cent.

*Cuminylidene-1-bromo-2-naphthylamine* forms sulphur-yellow needles and melts at 100—101°.

Its *hydrocyanide* separates from a mixture of benzene and light petroleum in transparent, colourless leaflets and melts at 120°; it darkens on exposure to the atmosphere.

0.2220 gave 14.1 c.c. moist nitrogen at 16° and 766 mm. N = 7.46.

$C_{21}H_{19}N_2Br$  requires N = 7.58 per cent.

*p-Hydroxybenzylidene-1-bromo-2-naphthylamine* crystallises from chloroform in pale yellow leaflets melting at 189—190°.

0.1400 gave 0.0820 AgBr. Br = 24.00.

$C_{17}H_{12}ONBr$  requires Br = 24.54 per cent.

The *hydrocyanide* crystallises from benzene in colourless, rhombic plates; it melts and decomposes at 143—144°.

*o-Hydroxybenzylidene-1-bromo-2-naphthylamine* crystallises from benzene and light petroleum in orange-yellow leaflets, and from dilute solutions in alcohol in large, orange, tabular prisms melting at 144° (compare Michaelis, *Annalen*, 1893, 274, 257). Its *hydrocyanide* crystallises from benzene in colourless, nacreous leaflets melting at 152°; on exposure to light, it becomes tinged with violet.

*p-Methoxybenzylidene-1-bromo-2-naphthylamine* crystallises from benzene in pale yellow leaflets and melts at 107°. Its *hydrocyanide* is readily soluble in the ordinary organic solvents, and crystallises from a mixture of benzene and light petroleum in well defined, opaque,

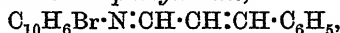


white needles. When rapidly heated, it melts at  $150-151^{\circ}$ , but when the temperature is gradually raised it darkens and decomposes at  $140-143^{\circ}$ , giving off hydrogen cyanide.

0.1780 gave 11.9 c.c. moist nitrogen at  $15^{\circ}$  and 746 mm.  $N=7.68$ .

$C_{19}H_{15}ON_2Br$  requires  $N=7.62$  per cent.

*Cinnamylidene-1-bromo-2-naphthylamine*,



readily dissolves in benzene, alcohol, or chloroform, but is less soluble in light petroleum; it crystallises in golden-yellow needles and melts at  $126^{\circ}$ .

0.1528 gave 0.0840 AgBr.  $Br=23.90$ .

$C_{19}H_{14}NBr$  requires  $Br=23.81$  per cent.

The *hydrocyanide*, which is rapidly produced from the preceding compound by the action of hydrogen cyanide, crystallises from benzene in white, lustrous leaflets melting at  $142-143^{\circ}$ .

*Benzylidene-1-chloro-2-naphthylamine* crystallises from light petroleum in pale yellow leaflets melting at  $98-99^{\circ}$ .

0.1041 gave 0.0584 AgCl.  $Cl=13.87$ .

$C_{17}H_{12}NCl$  requires  $Cl=13.37$  per cent.

The *hydrocyanide* crystallises in convoluted aggregates of small scales and melts at  $76-77^{\circ}$ .

0.2329 gave 19.2 c.c. moist nitrogen at  $16^{\circ}$  and 761 mm.  $N=9.62$ .

$C_{18}H_{13}N_2Cl$  requires  $N=9.57$  per cent.

*Cumylidene-1-chloro-2-naphthylamine* slowly separates in brown crusts on allowing the glacial acetic acid solution of its generators to evaporate at the ordinary temperature; when purified by crystallisation from light petroleum, it forms brownish-yellow leaflets melting at  $85^{\circ}$ .

0.1435 gave 0.0641 AgCl.  $Cl=11.06$ .

$C_{20}H_{13}NCl$  requires  $Cl=11.54$  per cent.

The *hydrocyanide* crystallises from methyl alcohol in transparent, colourless leaflets and melts at  $117^{\circ}$ .

0.1485 gave 10.9 c.c. moist nitrogen at  $16^{\circ}$  and 760 mm.  $N=8.64$ .

$C_{21}H_{19}N_2Cl$  requires  $N=8.37$  per cent.

*Cinnamylidene-1-chloro-2-naphthylamine*, like the corresponding bromine analogue, crystallises from benzene in golden-yellow needles; it melts at  $133-134^{\circ}$ .

0.1496 gave 0.0727 AgCl.  $Cl=12.00$ .

$C_{19}H_{14}NCl$  requires  $Cl=12.17$  per cent.

The *hydrocyanide* crystallises from methyl alcohol in lustrous, colourless leaflets, and melts at 155—156°.

0.1263 gave 10.0 c.c. moist nitrogen at 15° and 744 mm.  $N = 9.07$ .

$C_{20}H_{15}N_2Cl$  requires  $N = 8.79$  per cent.

*p-Hydroxybenzylidene-1-chloro-2-naphthylamine* is somewhat sparingly soluble in organic solvents other than chloroform; it crystallises in pale yellow, nacreous leaflets melting at 191°. The *hydrocyanide* crystallises from benzene in colourless, rhombic plates, and melts at 151—152°.

*p-Methoxybenzylidene-1-chloro-2-naphthylamine* crystallises from benzene in yellow leaflets and melts at 116—117°. The *hydrocyanide* forms well-defined, semi-opaque, white needles which gradually become tinged with green; it melts at 132°.

0.1378 gave 10 c.c. moist nitrogen at 16° and 766 mm.  $N = 8.52$ .

$C_{19}H_{15}ONCl$  requires  $N = 8.68$  per cent.

*o-Hydroxybenzylidene-1-chloro-2-naphthylamine* closely resembles the corresponding bromo-derivative, crystallising from benzene in orange leaflets, and from alcohol in large, orange, tabular prisms; it melts at 152—153°. Its *hydrocyanide* forms white, nacreous leaflets; these darken at 140°, and melt at 148°.

#### *Anhydro-bases derived from Nitrobenzaldehyde.*

*o-Nitrobenzylidene-1-bromo-2-naphthylamine* is readily obtained by the general method of preparation, and is readily soluble in all the ordinary organic solvents excepting light petroleum. It crystallises from a mixture of benzene and light petroleum in transparent, golden-yellow needles, and melts at 137—138°.

0.1808 gave 0.0945 AgBr.  $Br = 22.24$ .

$C_{17}H_{11}O_2N_2Br$  requires  $Br = 22.53$  per cent.

*p-Nitrobenzylidene-1-bromo-2-naphthylamine* resembles its *o*-isomeride, and melts at 154—155°.

*o-Nitrobenzylidene-1-chloro-2-naphthylamine* crystallises in golden-yellow needles and melts at 142°.

0.1730 gave 0.0782 AgCl.  $Cl = 11.17$ .

$C_{17}H_{11}O_2N_2Cl$  requires  $Cl = 11.43$  per cent.

*p-Nitrobenzylidene-1-chloro-2-naphthylamine* forms transparent, golden-yellow plates, and melts at 151°.

These four anhydro-bases containing nitro-groups do not react with hydrogen cyanide. When excess of hydrogen cyanide is added to a dry ethereal solution containing 1-bromo-2-naphthylamine, and the

mixture treated with *p*-nitrobenzaldehyde, also dissolved in ether, a yellow precipitate is produced consisting of the anhydro-base; the filtrate, after several days, yields a further quantity of this compound, but no trace of hydrocyanide.

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### CXV.—*Action of Hydrogen Peroxide on Carbohydrates in the Presence of Ferrous Salts. II.*

By ROBERT SELBY MORRELL, M.A., Ph.D., and JAMES MURRAY CROFTS, M.A., B.Sc.

IN a former paper (Trans., 1899, 75, 787), it was shown that hydrogen peroxide, in the presence of small quantities of ferrous sulphate, oxidises carbohydrates to osones. Oxidation by means of hydrogen peroxide in the presence of ferrous salts was first investigated by Fenton (Trans., 1894, 65, 899), and he has since examined its action on many polyhydric alcohols and hydroxy-acids (compare Trans., 1899, 75, 1; 1900, 77, 69, &c.).

The osones were detected as products of the oxidation of the carbohydrates by hydrogen peroxide by precipitating them as osazones by phenylhydrazine at the ordinary temperature, but it has been found advisable to remove the osone from the solution as the lead hydroxide compound (Fischer, *Ber.*, 1889, 22, 87). When baryta is added to a solution of an osone in the presence of basic lead acetate, the lead hydroxide which is precipitated carries down all the osone with it. It is then quite easy to liberate the osone by means of dilute sulphuric acid, and to obtain a solution which reacts with hydrazines at the ordinary temperature and does not ferment with yeast.

Glucose, lævulose, arabinose, and rhamnose have been oxidised by hydrogen peroxide in the presence of small quantities of ferrous sulphate, the osones removed from the solution by means of lead hydroxide and identified by means of their osazones. The osazones were always prepared by the action of phenylhydrazine at the ordinary temperature. In the case of arabinose, the solution was warmed to 60° so as to obtain the osazone precipitate in a more granular form, but this is allowable, since it has been shown that arabinose is more easily oxidised by hydrogen peroxide than glucose (Trans., 1899, 75, 792).

Galactose seems to behave abnormally on oxidation. A red substance, very soluble in alcohol and ether, is precipitated by phenyl-

hydrazine at the ordinary temperature. Attempts to purify it have been unsuccessful. Most probably the oxidation of the galactose proceeds further than the osone stage, giving rise to products which are of an acid nature and react readily with phenylhydrazine. The stereochemical arrangement of the  $\text{CH}\cdot\text{OH}$  groups in galactose may be referred to as an explanation of the failure to detect galactosone; moreover, the identity of the osazone obtained from galactosone with galactosazone is uncertain (Fischer, *Ber.*, 1889, 22, 96).

Applying the method of oxidation by hydrogen peroxide in the presence of ferrous sulphate to cane sugar, it has been found that using *neutralised* hydrogen peroxide the carbohydrate is first 'inverted,' and the glucose and lævulose formed are then oxidised to glucosone.

The action of potassium persulphate on glucose in the presence of ferrous sulphate is like that of hydrogen peroxide. The oxidation is very slow at the ordinary temperature, being most rapid at  $40^\circ$ . The yield of glucosone is much smaller than when hydrogen peroxide is the oxidising agent. The results of the action of bromine water on glucosone obtained from lævulose will be given in a subsequent paper.

#### EXPERIMENTAL.

##### *Rhamnose.*

A 10 per cent. aqueous solution of rhamnose containing 0.6 per cent. of ferrous sulphate is oxidised by hydrogen peroxide in the usual manner. The rhamnosone is precipitated with lead hydroxide, and after removal of the lead by dilute sulphuric acid, sodium acetate is added in excess and then a solution of phenylhydrazine acetate. The weight of rhamnosazone precipitated at the ordinary temperature varies from 20 to 35 per cent. of the weight of the rhamnose taken. On recrystallisation from dilute alcohol, the rhamnosazone melted at  $179\text{--}180^\circ$  with decomposition. After drying in a vacuum, the substance was analysed.

0.1734 gave 0.4029  $\text{CO}_2$  and 0.1061  $\text{H}_2\text{O}$ .  $\text{C} = 63.36$ ;  $\text{H} = 6.7$ .

0.1875 „ 26.8 c.c. moist nitrogen at  $16^\circ$  and 753 mm.  $\text{N} = 16.5$ .

$\text{C}_{18}\text{H}_{22}\text{O}_3\text{N}_4$  requires  $\text{C} = 63.2$ ;  $\text{H} = 6.43$ ;  $\text{N} = 16.37$  per cent.

##### *Cane Sugar.*

A 40 per cent. aqueous solution of cane sugar containing 0.2 per cent. of ferrous sulphate is oxidised by neutralised hydrogen peroxide in the usual manner. At first the action is slow and is accelerated by the addition of normal lead acetate after the first 1/10 atom of oxygen per molecule of cane sugar has been added. A quantity of hydrogen peroxide corresponding to 2 atoms of oxygen for a

molecular weight of cane sugar is used. Basic lead acetate is added, the liquid filtered, the lead removed exactly by dilute sulphuric acid, and the glucosazone precipitated by phenylhydrazine at the ordinary temperature. The filtrate on warming to  $50^{\circ}$  gave a further quantity of glucosazone. The yield is about 30 per cent. of the weight of the cane sugar taken.

The substance after recrystallising twice from absolute alcohol melted at  $205^{\circ}$  with decomposition and, after drying at  $105^{\circ}$ , gave on analysis the following numbers :

0.1892 gave 0.417  $\text{CO}_2$  and 0.107  $\text{H}_2\text{O}$ .  $\text{C} = 60.1$  ;  $\text{H} = 6.2$ .

0.18     ,,     24 c.c. moist nitrogen at  $14.5^{\circ}$  and 752 mm.  $\text{N} = 15.5$ .

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$  requires  $\text{C} = 60.3$  ;  $\text{H} = 6.1$  ;  $\text{N} = 15.6$  per cent.

#### *Action of Potassium Persulphate on Glucose.*

A 10 per cent. aqueous solution of glucose containing 0.8 per cent. of ferrous sulphate is treated with a quantity of solid potassium persulphate sufficient to provide one atom of active oxygen per gram-molecule of sugar. The solution is warmed at  $40^{\circ}$  until the ferric iron formed begins to be reduced to the ferrous state ; it is then allowed to stand at the ordinary temperature for some hours and afterwards treated with basic lead acetate, filtered, the lead removed from the filtrate by sulphuric acid, and the glucosazone precipitated at the ordinary temperature on addition of phenylhydrazine acetate. The yield of the osazone is 6 grams from 25 grams of glucose.

On recrystallisation from alcohol, the melting point was found to be  $205^{\circ}$ , and a nitrogen determination in a specimen dried at  $100^{\circ}$  gave the following numbers :

0.1725 gave 23 c.c. moist nitrogen at  $15^{\circ}$  and 760 mm.  $\text{N} = 15.35$ .

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$  requires  $\text{N} = 15.6$  per cent.

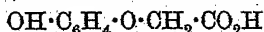
The authors wish to state that this research was carried out with the aid of a grant from the Chemical Society Research Fund and that they are indebted to Mr. F. M. Oldham for assistance in the experimental work.

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CXVI.—*The Hydroxyphenoxy- and Phenylenedioxy-acetic Acids.*

By W. CARTER and W. TREVOR LAWRENCE, B.A., Ph.D.

FOR many years, the sole representative of the important series of aromatic compounds represented by the general formula



was resorcinoldiacetic acid (*m*-phenylenedioxydiacetic acid) (Gabriel, *Ber.*, 1879, 12, 1640).

During the last few months, catecholacetic acid (*o*-hydroxyphenoxy-acetic acid) and its derivatives have formed the subject of careful investigation (compare Majert, D.R.-P. 87336, 87668, 87669; G. Tobias, D.R.-P. 89593; Moureu, *Bull. Soc. Chim.*, 1899, [iii], 21, 107; Ludewig, *J. pr. Chem.*, 1900, [ii], 61, 345; Lederer, D.R.-P. 108241), and still more recently Bischoff has published the results of researches on the condensation of catechol, resorcinol, and quinol with higher homologues of acetic acid (Bischoff, *Ber.*, 1900, 33, 1668, 1676, 1688).

The original intention of the authors was to prepare and investigate the mono- and di-acetic acid derivatives of the three dihydroxybenzenes, and to include in this investigation the formation of anhydrides, of nitro-derivatives, of amines, and of the morpholines and hydroxy-compounds derivable from these amines. Meanwhile, however, Prof. C. A. Bischoff, in answer to a communication, expressed a desire to reserve to himself the investigation of the compounds of resorcinol and quinol and we have consequently yielded to the request. This paper contains various data for the preparation and identification of the various acids, which may prove useful in determining the constitution of acids obtained by the oxidation of natural colouring matters, &c.\*

The general method of preparation of the acids forming the subject of this paper consists in heating the disodium dihydroxybenzene with two equivalents of ethyl chloro- or bromo-acetate in alcoholic solution until neutrality is obtained, an operation which requires about 5 hours. The product, in ethereal solution, is extracted first with a solution of potassium hydroxide, which removes unchanged dihydroxybenzene; the monoacetic acid derivative and the neutral ethers are then purified by fractional distillation in a vacuum, and hydrolysed by alcoholic potash; the potassium salts are precipitated at once, and on acidifying yield the pure acids which are recrystallised from water or acetic acid.

The monoacetic acids, to the extent of 10 per cent. of the theoretical

\*P. G. Gilbody, Perkin, and Yates obtained the acid  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , a monoacetic acid, from brazilin (*Proc.*, 1900, 16, 106).

yield, are obtained on acidifying the potash washings, and are freed from dihydroxybenzenes by solution in sodium carbonate. The only exceptions to the above generalisation are catechol, which is completely converted into the di-derivative; and quinol, the neutral ether of which crystallises easily, and is best purified by recrystallisation.

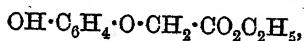
The acids crystallise with water, and in many cases exhibit dimorphism; thus *m*-phenylenedioxyacetic acid (resorcinoldiacetic acid) crystallises in needles from saturated aqueous solutions, and in prisms from dilute solutions. With the exception of *o*-hydroxyphenoxyacetic acid (catecholacetic acid), they give no coloration with ferric chloride; the salts of the di-acids are very sparingly soluble, but those of the mono-acids more soluble in water.

The di-acids may be equally well prepared by evaporating an aqueous solution of the disodium dihydroxybenzene with two equivalents of sodium chloroacetate.

#### *Catechol Derivatives.*

As the monoacetic acid derivative was not obtained as a bye-product in the preparation of the di-derivative, a condensation between monosodium catechol and one equivalent of ethyl chloroacetate was investigated in order to compare the results with those obtained by Moureu, Ludewig, and others; these agreed entirely, and will consequently only be summarised here.

Ethyl *o*-hydroxyphenoxyacetate (ethyl catecholacetate),



boiled at 155–156° under 30 mm. pressure. The corresponding acid, recrystallised from water, melted at 152°. Both the acid and the

ester are converted on distillation into the anhydride,  $\text{C}_6\text{H}_4 \begin{matrix} \text{O} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CO} \end{matrix}$ ,

which crystallises from light petroleum in prisms and melts at 57°. The anilide obtained from the anhydride and aniline melts at 165°.

*o*-Phenylenedioxydiacetic Acid.—When the ethereal solution of the product of the condensation of 1 mol. of disodium catechol with 2 mols. of ethyl bromoacetate was agitated with potash, about 50 per cent. went into solution, and was expected to consist of the monoacetic acid derivative; on acidifying the potash solution, a white, crystalline solid was precipitated, which crystallised from water and melted at 265°; it contained potassium, and was identical with the potassium hydrogen salt described on p. 1224.

*Ethyl o*-Phenylenedioxydiacetate,  $\text{C}_6\text{H}_4(\text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{C}_2\text{H}_5)_2$ , is a colourless, pleasant smelling liquid boiling at 230–232° under 32 mm. pressure.

The ester was hydrolysed by pouring into a solution of potash in

alcohol, the mixture becoming very hot, with immediate separation of the potassium salt. This was collected on the pump, washed, dried at  $100^{\circ}$ , dissolved in water, and acidified. The substance precipitated was recrystallised from water, from which it separated in fine needles melting at  $263^{\circ}$ ; it contained potassium, and the analyses, which did not agree very well, suggested that it was potassium hydrogen *o*-phenylenedioxydiacetate,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$ . The substance was very stable, and was not easily decomposed by boiling hydrochloric acid; it was consequently thought advisable to adopt another hydrolysing agent in place of caustic potash.

Ethyl *o*-phenylenedioxydiacetate is easily hydrolysed by boiling with hydrochloric acid, the solution solidifying on cooling to a mass of crystals which, on recrystallisation from water, melt at  $178^{\circ}$ , and consist of *o*-phenylenedioxydiacetic acid,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ .

0.0961 gave 0.1758  $\text{CO}_2$  and 0.0426 H. C = 49.9; H = 4.9.

0.1430 ,, 0.2624  $\text{CO}_2$  ,, 0.0631 H. C = 50.0; H = 4.9.

$\text{C}_{10}\text{H}_{10}\text{O}_6, \text{H}_2\text{O}$  requires C = 49.5; H = 4.9 per cent.

The calcium and barium salts of this acid are obtained as crystalline precipitates on addition of calcium or barium chloride to the solution of the ammonium salt. The barium salt was analysed, with the following result:

0.2372 lost 0.0007 at  $160^{\circ}$  and gave 0.1520  $\text{BaSO}_4$ . Ba = 37.8.

$\text{C}_{10}\text{H}_8\text{O}_6\text{Ba}, \frac{1}{2}\text{H}_2\text{O}$  requires Ba = 37.9 per cent.

Ethyl *o*-phenylenedioxydiacetate, on treatment with excess of concentrated aqueous ammonia, is converted quantitatively into *o*-phenylenedioxydiacetamide,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$ , which crystallises in needles from hot water and melts at  $203^{\circ}$ .

0.1120 gave 11.6 c.c. nitrogen at  $16^{\circ}$  and 763 mm. N = 12.1.

$\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$  requires N = 12.5 per cent.

The aniline salt of *o*-phenylenedioxydiacetic acid is formed by boiling the acid with a solution of aniline in benzene; it may be recrystallised from benzene, and melts at  $250^{\circ}$ .

The anilide,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)_2$ , may be obtained from the aniline salt, or, more simply, by heating the acid with aniline at  $180^{\circ}$ ; it crystallises from benzene in needles and melts at  $196^{\circ}$ .

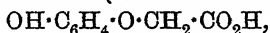
0.0958 gave 6.2 c.c. nitrogen at  $18^{\circ}$  and 756 mm. N = 7.4.

$\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_2$  requires N = 7.5 per cent.



*Resorcinol Derivatives.*

*m*-Hydroxyphenoxyacetic Acid (resorcinolacetic acid),



is obtained on acidifying the potash washings from the condensation product of disodium resorcinol and 2 mols. of ethyl bromoacetate, and extracting the acid solution with ether. It crystallises from water in small prisms, with  $\frac{1}{3}\text{H}_2\text{O}$ , melting at  $157\text{--}158^\circ$ , and from boiling toluene in needles melting at  $158\text{--}159^\circ$ .

0.1739 gave 0.3528  $\text{CO}_2$  and 0.0744  $\text{H}_2\text{O}$ .  $\text{C} = 55.2$ ;  $\text{H} = 4.8$ .

$\text{C}_8\text{H}_8\text{O}_4\cdot\frac{1}{3}\text{H}_2\text{O}$  requires  $\text{C} = 55.2$ ;  $\text{H} = 5.0$  per cent.

The *silver* salt was obtained by adding silver nitrate to the solution of the ammonium salt and crystallises in needles from water.

0.2101 gave 0.0896 Ag.  $\text{Ag} = 42.7$ .

$\text{C}_8\text{H}_7\text{O}_4\text{Ag}$  requires  $\text{Ag} = 43.0$  per cent.

The *anilide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , melts at  $125^\circ$ , and is obtained by heating the acid with aniline at  $180^\circ$ .

*Ethyl m*-Phenylenedioxydiacetate,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{C}_2\text{H}_5)_2$ , is formed both by the condensation of disodium resorcinol with 2 mols. of ethyl bromoacetate and by evaporation of an aqueous solution of disodium resorcinol with 2 mols. of chloroacetic acid dissolved in excess of caustic soda. It is obtained on fractional distillation of the products as a thick, colourless oil, which boils at  $228^\circ$  under 32 mm. pressure, and on standing for several weeks crystallises in needles melting at  $42^\circ$ .

The hydrolysis of the ester was carried out in the same manner as that of the catechol derivative, and *o*-phenylenedioxydiacetic acid,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , was obtained, crystallising from saturated aqueous or acetic acid solutions in fine needles melting at  $195^\circ$ , and from dilute solutions in prisms having the same melting point.

0.2436 gave 0.4700  $\text{CO}_2$  and 0.0897  $\text{H}_2\text{O}$ .  $\text{C} = 52.7$ ;  $\text{H} = 4.1$ .

$\text{C}_{10}\text{H}_{10}\text{O}_6$  requires  $\text{C} = 53.1$ ;  $\text{H} = 4.4$  per cent.

The *silver*, *copper*, and *iron* salts of this acid are obtained from the ammonium salt as amorphous precipitates, insoluble in water; the *barium* and *calcium* salts are crystalline, and are slightly soluble in boiling water.

The ester, on agitation with strong aqueous ammonia, is converted into *m*-phenylenedioxydiacetamide,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$ , which crystallises from water in needles melting at  $167^\circ$ .

0.0806 gave 8.6 c.c. nitrogen at  $17^\circ$  and 758 mm.  $\text{N} = 12.3$ .

$\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$  requires  $\text{N} = 12.5$  per cent.

If the ester is warmed with dilute ammonia solution, a substance crystallising in needles melting at  $43^{\circ}$  is formed. Possibly it has the constitution  $\text{NH}(\text{CO}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2 \text{C}_2\text{H}_5)_2$ .

0.1234 gave 3 c.c. nitrogen at  $21^{\circ}$  and 758 mm.  $N = 2.7$ .

$\text{C}_{24}\text{H}_{27}\text{O}_{10}\text{N}$  requires  $N = 2.9$  per cent.

The *aniline* salt is obtained by boiling the acid with aniline in benzene solution, and melts at  $137^{\circ}$ ; it may be recrystallised from benzene. On distillation, it is converted into *m*-phenylenedioxydiacetanilide,  $\text{C}_6\text{H}_4(\text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5)_2$ , which crystallises in prisms from benzene and melts at  $169^{\circ}$ ; the anilide may more easily be obtained by heating the acid with aniline at  $190^{\circ}$ .

0.1165 gave 7.5 c.c. of nitrogen at  $18^{\circ}$  and 756 mm.  $N = 7.4$ .

$\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_2$  requires  $N = 7.5$  per cent.

On boiling *m*-phenylenedioxydiacetic acid with fuming nitric acid diluted with half its volume of water, *trinitro-m*-phenylenedioxydiacetic acid,  $(\text{NO}_2)_3\text{C}_6\text{H}(\text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$ , is formed and crystallises from the solution on cooling in pale yellow prisms which may be purified by recrystallisation from water, and melt at  $174^{\circ}$ .

0.1637 gave 17 c.c. nitrogen at  $19^{\circ}$  and 751 mm.  $N = 11.7$ .

$\text{C}_{10}\text{H}_7\text{O}_{12}\text{N}_3$  requires  $N = 11.7$  per cent.

This nitro-compound is converted by potash at  $140^{\circ}$  into styphnic acid (2:4:6-trinitroresorcinol), and is consequently the 2:4:6-trinitro-derivative.

### Quinol Derivatives.

*p*-Hydroxyphenoxyacetic Acid,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is obtained in the same way as the corresponding resorcinol derivative. It crystallises from water in prisms with  $\frac{1}{3}\text{H}_2\text{O}$ , and from toluene or xylene in anhydrous needles, both forms melting at  $152^{\circ}$ .

0.2738 gave 0.5560  $\text{CO}_2$  and 0.1247  $\text{H}_2\text{O}$ .  $C = 55.3$ ;  $H = 5.0$ .

$\text{C}_8\text{H}_5\text{O}_4 \cdot \frac{1}{3}\text{H}_2\text{O}$  requires  $C = 55.2$ ;  $H = 5.0$  per cent.

After crystallisation from xylene,

0.3418 gave 0.7132  $\text{CO}_2$  and 0.1459  $\text{H}_2\text{O}$ .  $C = 57.1$ ;  $H = 4.7$ .

$\text{C}_8\text{H}_5\text{O}_4$  requires  $C = 57.1$ ;  $H = 4.7$  per cent.

The *aniline* salt melts at  $119^{\circ}$ .

The *anilide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ , crystallises in prisms from benzene and melts at  $101^{\circ}$ .

0.1463 gave 7.1 c.c. nitrogen at  $22^{\circ}$  and 763 mm.  $N = 5.7$ .

$\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}$  requires  $N = 5.8$  per cent.

*Ethyl p-Phenylenedioxydiacetate*,  $C_6H_4(O \cdot CH_2 \cdot CO_2C_2H_5)_2$ —The ethereal solution from the condensation of 1 mol. of disodium quinol with 2 mols. of ethyl bromoacetate, after washing with potash, begins to crystallise, and on distilling off the ether, a solid cake of ethyl *p*-phenylenedioxydiacetate is obtained. When recrystallised from dilute alcohol or light petroleum, the ester melts at  $72^\circ$ .

0.1713 gave 0.3747  $CO_2$  and 0.0994  $H_2O$ .  $C = 59.6$ ;  $H = 6.4$ .

$C_{14}H_{18}O_6$  requires  $C = 59.5$ ;  $H = 6.3$  per cent.

The crystalline ester is converted on hydrolysis with alcoholic potash into *p-phenylenedioxydiacetic acid*,  $C_6H_4(O \cdot CH_2 \cdot CO_2H)_2$ , which melts at  $251^\circ$ , and is very sparingly soluble in all solvents, but may be obtained as a microcrystalline powder from boiling acetic acid.

0.2394 gave 0.4640  $CO_2$  and 0.0996  $H_2O$ .  $C = 52.3$ ;  $H = 4.6$ .

$C_{10}H_{10}O_6$  requires  $C = 53$ ;  $H = 4.4$  per cent.

On neutralising the acid with ammonia, the *ammonium* salt is formed, which crystallises from water in needles; its solution gives amorphous precipitates with silver, copper, and iron salts, and crystalline precipitates with barium and calcium salts. The *barium* salt was analysed with the following result:

0.3660 lost 0.0011 at  $160^\circ$ , and gave 0.2324  $BaSO_4$ .  $Ba = 37.4$ .

$C_{10}H_8O_6Ba, \frac{1}{3}H_2O$  requires  $Ba = 37.9$  per cent.

The *anilide*,  $C_6H_4(O \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_5)_2$ , crystallises in glistening needles from benzene and melts at  $210^\circ$ .

0.1617 gave 10.3 c.c. nitrogen at  $18^\circ$  and 756 mm.  $N = 7.3$ .

$C_{22}H_{20}O_4N_2$  requires  $N = 7.5$  per cent.

The investigations of Prof. C. A. Bischoff (compare *Ber.*, 1900, 33, 924) having been confined to acids of the type  $C_6H_4(O \cdot CRR' \cdot CO_2H)_2$ , we concluded he had, with intention, omitted the study of the acetic acid derivatives. We communicated with him, however, and in a letter dated May 26th he announced his intention of investigating the acetic acid derivatives of resorcinol and quinol, and, subsequently to the abstract of this paper being communicated to the Society, a notice to this effect has appeared in the *Berichte* (*loc. cit.*, 1692).

CXVII.—*Specific Gravities of the Halogens at their Boiling Points, and of Oxygen and Nitrogen.*

By JULIEN DRUGMAN, Ph.D., and WILLIAM RAMSAY, F.R.S.

THE object of the following experiments was to determine the specific gravities of the halogens in the liquid state under similar conditions. The conditions chosen were the boiling points of the elements under atmospheric pressure, as from Young's experiments (Ramsay and Young, *Phil. Mag.*, 1885, [v], 20, 518; Young, *Phil. Mag.*, 1892, 33, 161; 1894, 37, 4) the benzene halides have molecular volumes at the boiling point under equal pressures which bear constant ratios to one another for all equal pressures, and therefore also for their critical pressures.

If similar halides have these properties, it is reasonable to expect that the halogens would also bear the same ratios to one another, and that the densities at their boiling points would bear the same ratios under the ordinary atmospheric pressure as at their critical pressure.

The specific gravity of iodine was first determined. For this purpose, a small glass bulb with a capillary tube bent twice at right angles was used. Its capacity was accurately determined, and then it was filled with liquid iodine by heating, dipping the end of the capillary in liquid iodine, and afterwards letting it cool.

The bulb was then hung up by means of a wire in a wide tube about 18 inches in length containing boiling iodine, and left there long enough to get heated to the same temperature as the vapours from the boiling iodine. It was now quickly drawn out, allowed to cool, and the weight of the iodine left in it determined. The following results were obtained:

	Temperature.	Volume of bulb.	Weight of iodine.	Sp. gr. iodine.
1.	184.5°	2.326 c.c.	8.6200 gr.	3.706
2.	184.3°	1.763 „	6.5384 „	3.708
3.	184.5°	2.042 „	7.5550 „	3.699

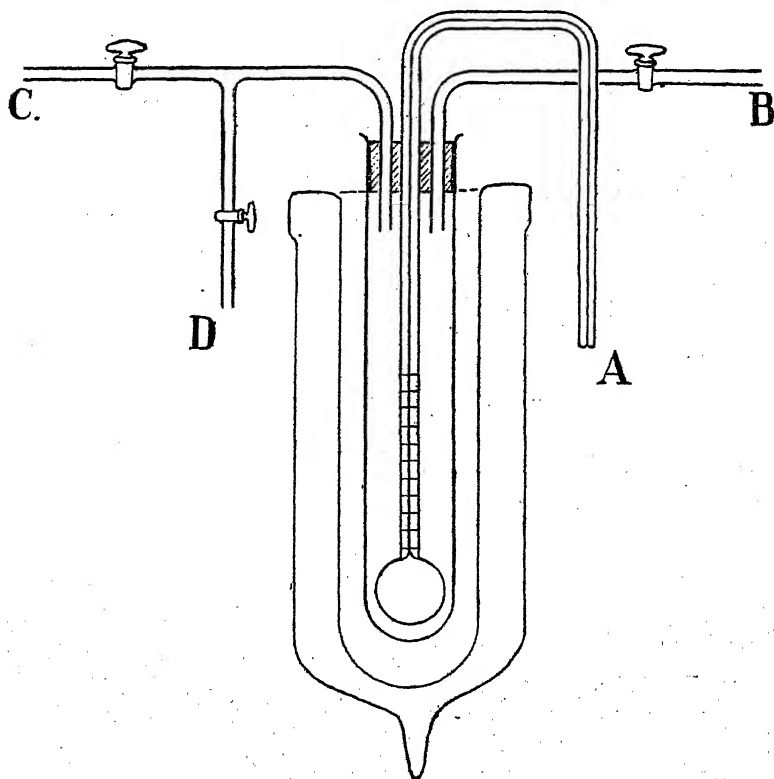
No. 3 was too low owing to a piece of the capillary containing some iodine having cracked off on cooling. The average would then be 3.706 at a temperature of about 184.35°, that is, the boiling point under 760 mm. (Ramsay and Young, *Trans.*, 1886, 49, 461).

In determining the volume of the bulb, the expansion of the glass was taken into account, and in all the following determinations the expansion or contraction of the bulb was allowed for. The coefficient used was 0.000025 for the temperatures above zero, and 0.0000219 at lower temperatures (Baly, *Phil. Mag.*, 1900, [v], 49, 518).

The specific gravity of bromine under similar conditions having already been found, that of chlorine was next determined.

The apparatus for chlorine was necessarily more complicated, but the method was the same as that just described, that is, heating a bulb containing the liquid by means of the vapours of the same liquid boiling in an outer jacket at atmospheric pressure, and then determining the weight of the contents of the bulb.

The bulb was in this case an ordinary thermometer bulb with the



stem bent twice at right angles, and graduated for 2 or 3 inches from the bulb upwards. The weight of the chlorine was determined by absorbing the gas in potassium iodide solution and titrating the liberated iodine with thiosulphate solution.

The bulb and jacket were exhausted several times by means of an air-pump. The accompanying diagram shows the apparatus used. A was first connected to a T-tube leading on one side to the vacuum pump, and on the other to the chlorine generator;

afterwards the T-tube was removed and replaced by the potassium iodide absorption apparatus. B connected the jacket with another chlorine generator, C with the vacuum pump, D with an absorption apparatus containing slaked lime and open at one end to the outer atmosphere in order that atmospheric pressure should be maintained in it.

By means of liquid air, chlorine was first condensed in the jacket until it was half full of liquid, and, at that temperature, solid chlorine. Then the gas was allowed to condense in the inner bulb. The liquid air was now replaced by an empty cooled vacuum tube, and while the temperature of the chlorine rose slowly to the boiling point, A was connected with the potassium iodide apparatus, and as soon as the liquid had fully expanded in the bulb its height was read.

The vapour jacket not only insures correctness of temperature, but in cases like the above prevents any sudden boiling up of the liquid before the readings have been taken.

The following results were found :

Volume of bulb, 0.579 c.c.

Weight of iodine liberated, 3.1215.

Weight of the chlorine, 0.8725 gr.

Sp. gr., 1.5071 at  $-33.6^{\circ}$ .

The values hitherto found for the specific gravity of chlorine are 1.33 at  $15^{\circ}$  under 4 atmospheres pressure, and 1.56 at a temperature below the boiling point.

Fluorine is the only halogen whose specific gravity at its boiling point has still to be determined, but owing to the difficulties attending the practical carrying out of the determination use was made of the data given by Moissan and Dewar (*Proc.*, 1897, 13, 180). They give the boiling point of fluorine as being slightly lower than that of oxygen, about  $-187^{\circ}$ . Its density they determined by putting substances of known density in a tube cooled to  $190^{\circ}$  and condensing the fluorine in it. Amber was found to agree almost exactly in density with the fluorine. They also remark that fluorine contracts about  $1/14$ th of its volume from this temperature to  $-210^{\circ}$ , that is, for a difference in temperature of about  $20^{\circ}$ .

First the density of amber at a temperature near that of boiling fluorine was determined by finding its loss of weight in liquid oxygen kept at a temperature just below the boiling point. For this purpose, the density of the oxygen was also ascertained, as it has not been determined yet at the boiling point under ordinary pressure with sufficient accuracy.

The apparatus as that used for chlorine was employed,

replacing the chlorine generators by oxygen holders, and the absorption apparatus by a gas-measuring apparatus.

The purity of the oxygen in the outer tube was not of such importance so long as its temperature was exactly known; Brin's oxygen containing 93—95 per cent. of oxygen was therefore used, and its boiling point deducted from Baly's curve (*loc. cit.*). At the pressures of 759—762 mm., the boiling point is  $89.4^{\circ}$  to  $89.7^{\circ}$  absolute, or  $-183.6^{\circ}$  to  $-183.3^{\circ}$ .

The following results were found :

	Temperature.	Volume of bulb.	Weight of oxygen.	Density.
1.	$-183.6^{\circ}$	2.093 c.c.	2.3692 gr.	1.1321
2.	$-183.3$	0.913 „	1.0326 „	1.1310

These are slightly lower than those given by Dewar (1.1378 at 776.5 mm.), but as he does not seem to have used an oxygen jacket but liquid air to surround his vessel, the temperature during his determination must have been rather lower.

Amber was now cooled in liquid air, and then dropped into liquid oxygen in a small vacuum vessel, enclosed in a second one containing liquid air. In air it sank, but in the oxygen it rose to the surface, showing it to be lighter than liquid oxygen at that temperature.

By weighting the amber with a piece of silver whose density in the oxygen had been determined, the density of the amber was also determined and found to be 1.100 for a piece of amber of 1.065 density at  $15^{\circ}$ , that is, a difference of 0.035 for a lowering in temperature of  $200^{\circ}$ .

The accuracy would be great enough in taking 1.11 as the average density of amber at  $-190^{\circ}$ , and allowing for an expansion of the fluorine of about 1/90th of its volume from  $-190^{\circ}$  to  $-187^{\circ}$ , we can take its density at its boiling point to be about 1.108; an accurate determination is, however, not possible from the data given by Moissan and Dewar, and so the above can only be taken as a rough approximation.

As the densities of liquefied gases have given somewhat different results in later experiments, and as that of nitrogen does not seem to have been determined lately, it was also measured under the same conditions as the others in this paper. In this case, the vapour jacket was dispensed with, and so the results do not agree very closely, probably owing to the ease with which the nitrogen gets superheated, as Baly mentions in his paper on the vapour pressures of nitrogen. Both chemically pure nitrogen and atmospheric nitrogen were used, and, although the average density was slightly higher in the case of the latter, the accuracy of the determinations

was not great enough to find the exact difference in the density of the chemically pure and the atmospheric nitrogen.

For this purpose, the nitrogen vapour jacket should have been used and the bulb should have been larger. That used was only 1.52 c.c. in capacity; a bulb of about 3—5 c.c. should give accurate results. The following results were obtained:

*A. Chemical nitrogen.*

Temperature.	Vol. of bulb.	Weight of nitrogen.	Sp. gr.
1. -195.5°	1.522 c.c.	1.1938 gr.	0.7843
2. -195.6	1.531 „	1.2116 „	0.7914

*B. Atmospheric nitrogen.*

3. -195.5°	1.531 c.c.	1.2026 gr.	0.7855
4. -195.5	1.541 „	1.2205 „	0.7920
5. -195.5	1.537 „	1.2158 „	0.7908

In Nos. 1 and 3, 0.7843 and 0.7855, the nitrogen seems to have been superheated, as these results are rather far apart from the others. The average for the density of nitrogen at its boiling point under ordinary pressure, that is, at -195.5° under 760 mm., is then 0.7914. This is much lower than the values given by Wróblewski (0.83 under 1 atmosphere) and Olszewski (0.886 under 748 mm., and 0.859 under 740.9 mm. pressure).

These data enable us to compare the molecular volumes of a number of elements. The specific volumes of the elements under investigation are:

	Sp. vol.	Mol. vol.
Nitrogen .....	1.390	39.04
Phosphorus .....	0.6734	41.82
Oxygen.....	0.8838	28.28
Sulphur .....	0.6757	43.20
Fluorine .....	0.9025	34.30
Chlorine .....	0.6635	47.04
Bromine .....	0.3392	54.26
Iodine .....	0.2698	68.46

The atomic volume of nitrogen in combination has been given as 2.3 by Kopp from a single determination, that of aniline. One of us (Ramsay, Trans., 1881, 39, 67) showed that the value of nitrogen in amines is better taken as 7.0. This, however, would give the density of free nitrogen as 2, a result much in excess of the truth. It is interesting to compare the volumes of phosphorus and of sulphur in the free state and in combination. The results (Ramsay, Trans., 1881, 39, 67, and Thorpe, Trans., 1880, 37, 391) show that in



the free state sulphur has the lower of its two molecular volumes, namely, 22.6; and phosphorus has the atomic volume 20.7 in combination and 20.9 in the free state. The lower volume corresponds with that of pentad phosphorus, and presumably the volume of sulphur in the free state, with that of hexad sulphur. From analogy, the volume of free nitrogen should be that of pentad nitrogen, as, for instance, in the nitro-group; this corresponds with 17.4 in the free peroxide of nitrogen, as well as in combination, a number not differing very greatly from 19.52, the value of the atomic volume of free nitrogen.

### CXVIII.—*Hydroferrocyanic Acid.*

By KENDALL COLIN BROWNING, B.A.

AMONG the many apparently contradictory statements made concerning the properties of hydroferrocyanic acid, are those referring to the action of heat on the substance.

Robiquet (*Ann. Chim. Phys.*, 1819, [i], 12, 277) obtained anhydrous hydrocyanic acid by heating hydroferrocyanic acid to the boiling point of mercury. On further raising the temperature, nitrogen was evolved, and a black powder left, which, with caustic potash, gave a trace of potassium ferrocyanide, and on boiling evolved traces of ammonia. The residue was non-magnetic, contained carbon, and was regarded as a mixture of iron and carbon.

Berzelius (*Ann. Chim. Phys.*, 1820, [i], 15, 228) heated ammonium ferrocyanide and obtained iron cyanide. This substance, at a low red heat, evolved nitrogen and left iron carbide. No analyses are given in the paper.

Rammelsberg (*Pogg. Ann.*, 1851, 38, 364; 42, 111) states that by heating hydroferrocyanic acid he obtained ferrous cyanide, and at a "higher temperature" paracyanogen and a substance  $C_{10}N_5Fe_6$ .

Etard and Bémont (*Compt. rend.*, 1884, 99, 972, 1024) say that dry hydroferrocyanic acid at 440° evolves 46 per cent. of hydrocyanic acid, leaving a yellow mass,  $FeHFeCy_5$  or  $2FeCy_2.HCy$ .

The acid used in the following work was obtained by adding pure hydrochloric acid to a cold saturated solution of purified potassium ferrocyanide. It was dissolved in absolute alcohol, precipitated by dry ether, dried at 80–90° in hydrogen and then in a vacuum, and redissolved in absolute alcohol. This process was repeated five times, until potassium could no longer be detected spectroscopically.

The following results were obtained on analysis:

Found, Fe = 25.85, 25.80, 25.998. Calc., Fe = 26.04 per cent.

Thus obtained, the acid is a snow-white mass. It obstinately retains ether, and this is best removed by heating to  $80^{\circ}$  for some hours in a current of hydrogen dried by phosphoric oxide, and finally raising the temperature to  $100^{\circ}$ .

*Decomposition of Hydroferrocyanic Acid in Air.*

When dry and free from ether, hydroferrocyanic acid remains unchanged when exposed to air, over phosphoric oxide, for many months.

On gentle warming in air, it turns blue, evolving hydrocyanic acid, and when heated for a few days to just over  $100^{\circ}$ , it completely oxidises to ferric oxide. As would be expected, it deflagrates when mixed with sodium peroxide and gently warmed. When warmed to  $60^{\circ}$  with water free from air, it evolves hydrocyanic acid, leaving ferrous cyanide (compare Adie and Browning, Trans., 1900, 77, 150).

*Action on Ether.*

When dry hydroferrocyanic acid is treated with absolute ether, a considerable evolution of heat occurs, and the mass swells up. According to Etard and Bémont (*loc. cit.*), the compound  $\text{H}_4\text{FeCy}_6, 2\text{Et}_2\text{O}$  is obtained, but they give no analyses or details.

Dry hydroferrocyanic acid was therefore exposed to absolute ether vapour for a few weeks, and then kept in a desiccator over paraffin till the weight was approximately constant. Analyses gave:

Ether = 28.06 and 28.29 per cent.

$\text{H}_4\text{FeCy}_6, 2\text{Et}_2\text{O}$  requires ether = 40.66 per cent.

$\text{H}_4\text{FeCy}_6, \text{Et}_2\text{O}$  „ ether = 25.5 „

By very gently warming in dry air for some days, almost every trace of ether was expelled, so no very definite compound seems to exist under these conditions.

*Action of Heat in absence of Oxygen.*

The decomposition described below was effected in hard glass vessels which were heated in a bath of Wood's metal. Owing to the ease with which the products oxidise, the whole apparatus was repeatedly exhausted by a mercury pump, and filled with purified hydrogen dried by phosphoric oxide.

A manometer was used to show when gas evolution commenced, and afterwards a very slow current of hydrogen was passed to sweep out the last traces of hydrocyanic acid. Temperatures were taken by a mercury thermometer filled with nitrogen under pressure.

A very slow evolution of hydrocyanic acid begins at  $120^{\circ}$ , but even

when heated at  $220^{\circ}$  for 3 hours the decomposition is not complete, the product containing undecomposed hydroferrocyanic acid.

Found, Fe = 44.2 and 44.3 per cent.

$\text{FeCy}_2$  requires Fe = 51.8 per cent.

$\text{FeCy}_2 \cdot \text{HCy}$  „ Fe = 41.4 „

$2\text{FeCy}_2 \cdot \text{HCy}$  „ Fe = 46.1 „

At  $300^{\circ}$ , however, the decomposition was rapid, and was complete in less than two hours. The whole of the hydrocyanic acid was evolved and a pale yellow powder, which analysis showed to be ferrous cyanide, was left.

Found, Fe = 51.4, 51.2.  $\text{FeCy}_2$  requires Fe = 51.8 per cent.

The difference is undoubtedly due to the ease with which ferrous cyanide undergoes oxidation. Even in cold air it rapidly becomes warm, turning greenish-yellow, slate-blue, and finally deep blue, and when warmed gently, it glows, burning to ferric oxide.

This decomposition of hydroferrocyanic acid gives a convenient and moderately safe method of preparing dry, colourless hydrocyanic acid.

Ferrous cyanide is stable, in absence of oxygen, up to  $430^{\circ}$ , but above that temperature it very slowly evolves nitrogen. The evolution becomes more rapid on raising the temperature, but is not complete even after six hours heating at about  $480^{\circ}$ . For example, a specimen gave Fe = 67.3,  $\text{FeC}_2$  requiring Fe = 70 per cent.

By heating to dull redness in a lead-bath for 4 hours, all the nitrogen was evolved and a black mass left, which had a composition approximating to that required for the carbide  $\text{FeC}_2$ .

Found, Fe = 70.4, 70.7, 70.5.  $\text{FeC}_2$  requires Fe = 70.0 per cent.

The excess of iron seems due to slight reduction of the cyanide by the small amount of hydrogen present in the vessel.

The black mass left is a very fine powder, and when gently warmed it glows, oxidising to ferric oxide, hence great care must be taken to remove all oxygen from the apparatus in which the ferrous cyanide is prepared. It partially dissolves in dilute hydrochloric or sulphuric acids, evolving hydrogen and small quantities of hydrocarbons. With nitric acid of sp. gr. 1.35, it partially dissolves, giving the usual coffee-coloured solution, indicating the presence of a carbide. The substance, however, is not pure iron carbide,  $\text{FeC}_2$ , as

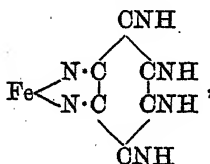
(i) It partially and readily dissolves in dilute hydrochloric acid, and the residue dried in a vacuum at  $160^{\circ}$ , or over phosphoric oxide in a vacuum for three weeks, only contains about 29 per cent. of iron (found, Fe = 29.0, 29.3 per cent.).

(ii) The residue left after repeated treatment with acid is pure carbon only. The carbide present is not due to reaction between the iron and carbon formed by decomposition of the cyanide, as by heating an intimate mixture of reduced iron and carbon powder for 3 hours at the temperature of complete decomposition of ferrous cyanide, no trace of carbide could be detected by the nitric acid reaction.

Hence it would seem that ferrous cyanide decomposes chiefly to iron, carbon, and iron carbide. The product contains no cyanide, but by treating with hydrochloric acid and then with caustic potash, a trace of ammonia was evolved, so apparently a trace of iron nitride is formed (compare Fowler, *B.A. Report*, 1893; *Abstr.*, 1894, ii, 50).

#### *Constitution of Ferrous Cyanide.*

According to Friedel's suggestion (note to a paper by Muller, *Compt. rend.*, 1887, 104, 994), hydroferrocyanic acid is



and, unless tautomeric change occurs in the decomposition, ferrous cyanide should be an *isocyanide*.

Although ferrous cyanide does not react with ethyl iodide even when heated with it and alcohol for many hours, yet when warmed in a current of hydrogen with potassium ethyl sulphate, ethyl *isocyanide* was obtained and was readily identified. This reaction would tend to confirm the *isocyanide* formula, as ethyl cyanide is not transformed to the *isocyanide* at the temperature used (200—220°).

Lastly, Wade (*Proc.*, 1900, 16, 156) has shown that the effect of heat is to transform a metallic *isocyanide* into the normal form, and not *vice versa*, just as is the case with many organic *isocyanides*. Wade finds that potassium cyanide is really an *isocyanide*, and undergoes transformation into the normal form on heating strongly; ferrous cyanide also behaves in a similar manner.

If ferrous cyanide were  $\text{Fe}(\text{CN})_2$ , then it would be expected to leave iron carbide when all nitrogen is expelled, whereas if it has the isomeric structure  $\text{Fe}(\text{NC})_2$ , it should give iron, carbon, and possibly a trace of nitride. As a matter of fact, the product is a mixture of iron, carbon, iron carbide, and possibly a trace of nitride, so it would seem that the ferrous cyanide group has the latter constitution in hydroferrocyanic acid, but when decomposing at about 500° behaves as if it were a mixture of the cyanide and *isocyanide*.

*Constitution of Hydroferrocyanic Acid.*

Owing to the ease with which a hydrogen atom shifts from one position to the other, it is almost impossible to decide from the behaviour of free hydrocyanic acid whether in hydroferrocyanic acid the four HCN groupings have the *iso*- or normal arrangement. Brühl (*Ber.*, 1883, 26, 806) states that, from its molecular refraction, hydrocyanic acid would seem to have a constitution different from that of cyanogen, which he has shown has a molecular refraction agreeing with that calculated for the constitution  $N:C\equiv N$ ; it must therefore be  $HN:C$  or  $HN\dot{C}$ . In a later paper, however (*Zeit. physikal. Chem.*, 1895, 16, 497), he concludes that the acid is  $HC\dot{N}$ , as its molecular refraction (for sodium light) agrees with that of the aliphatic cyanides.

The *isocyanide* formula is, however, supported by Neff's work on bivalent carbon (*Annalen*, 1892, 270, 267; 1895, 287, 265; compare also Thiele, *Ber.*, 1883, 26, 2645). For example, hydrocyanic acid readily combines with ethyl hypochlorite to form ethyl cyanimidocarbonate,  $C\dot{N}\cdot C(NH)\cdot OC_2H_5$ . Further, in presence of alcohol, it first forms (with hydrogen chloride) imidoformyl chloride,  $NH:CHCl$ , and then the compound  $NH:CH\cdot C(NH)Cl$ .

Kieseritzky (*Zeit. physikal. Chem.*, 1899, 23, 385), from the results obtained by an electrometric method of determining constitution, concludes that hydrocyanic acid is  $H\cdot N\dot{C}$ .

The above work, however, does not obviate the possibility of tautomerism, and indeed the fact that dry hydrocyanic acid is very inert and does not combine with chlorine or hydrogen chloride at low temperatures, or with ethyl hypochlorite at  $-10^\circ$ , tends to show that under some conditions hydrocyanic acid behaves as if it were  $H\cdot ON$ .

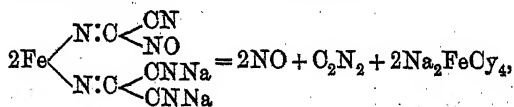
Hence it does not seem possible, from examination of the hydrocyanic acid prepared from hydroferrocyanic acid, to draw any very definite conclusion as to the constitution of the latter. The decomposition of ethyl ferrocyanide was therefore examined.

Ethyl ferrocyanide was first prepared by Freund (*Ber.*, 1888, 21, 931) by washing precipitated silver ferrocyanide with strong alcohol, and heating it, without further drying, with alcohol and ethyl iodide; the yield, however, is unsatisfactory. A better method is to dry silver ferrocyanide over phosphoric oxide in a vacuum, grind it to an impalpable powder, mix with twice its weight of dry sea-sand, and heat under pressure with absolute alcohol and slight excess of ethyl iodide for 12 hours at  $100^\circ$  (the yield is not improved by heating at  $130^\circ$  in an autoclave). The mass is then repeatedly extracted with absolute alcohol, evaporated down, recrystallised from chloroform, and dried in warm air, or recrystallised from excess of boiling acetone.

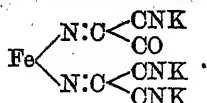
According to Freund, the ester decomposes on heating, giving ethyl isocyanide. His experiments were repeated, and confirmed in every detail. The free acid would therefore seem to be  $4\text{H}\cdot\text{NC}(\text{FeNC})_2$ , agreeing thus with Friedel's formula. In support of this ring formula, the stability of most ferrocyanides when heated may be quoted, but no other satisfactory evidence has been adduced. It does not, however, easily explain (i) the ready formation of nitroprussides by the action of nitric acid on ferrocyanides, or of nitroprussic acid by the action of nitric oxide on a warm aqueous solution of hydroferrocyanic acid (Playfair, *Phil. Mag.*, 1850, [iii], 36, 197, 271, 348), or by the action of potassium nitrite on ferricyanides at  $100^\circ$  (Prud'homme, *Compt. rend.*, 1890, 111, 45); (ii) the transformation of nitroprussides into ferrosotetracyanides on heating (Etard and Bémont, *Compt. rend.*, 1885, 100, 275),  $2\text{Na}_2\text{NOFeCy}_3 = 2\text{Na}_2\text{FeCy}_4 + 2\text{NO} + \text{C}_2\text{N}_2$ . If, however, we

assume that hydroferrocyanic acid is  $\text{Fe} \begin{matrix} \text{N:C} \begin{matrix} \text{CNH} \\ \text{CNH} \end{matrix} \\ \text{N:C} \begin{matrix} \text{CNH} \\ \text{CNH} \end{matrix} \end{matrix}$  then nitro-

prussides become salts of the acid  $\text{Fe} \begin{matrix} \text{N:C} \begin{matrix} \text{ON} \\ \text{NO} \end{matrix} \\ \text{N:C} \begin{matrix} \text{CNH} \\ \text{CNH} \end{matrix} \end{matrix}$ . Their decomposition, on heating, would be readily explained thus:



and potassium carbonylferrocyanide (Muller, *loc. cit.*) would be



The author has much pleasure in acknowledging Mr. Adie's help and suggestions throughout the course of this work.

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CXIX.—*The Nature of Metal-ammonia Compounds in Aqueous Solution. Part I.*

By H. M. DAWSON and J. MCCRAE.

REYCHLER (*Bull. Soc. Chim.*, 1895, [iii], 13, 387; *Ber.*, 1895, 28, 555) has shown that the freezing point of a solution of silver nitrate is not appreciably altered by the addition of 2 molecules of ammonia per molecule of salt, but that further addition of ammonia is accompanied by a considerable lowering of the freezing point. In the case of copper sulphate solutions, the freezing point is depressed to some extent by the addition of 4 molecules of ammonia per molecule of salt, whilst in the case of copper nitrate the addition of a similar quantity of ammonia produces very little change in the temperature at which ice separates from the solution. Similar results were obtained by him for the variation of the equivalent conductivity of solutions of silver nitrate, copper sulphate, and copper nitrate on the addition of corresponding quantities of ammonia.

From Reyehler's experiments, it is evident that the number of molecules present in the silver nitrate solution is not increased on the addition of 2 mols. of ammonia to 1 mol. of salt. When more ammonia is added, then the total number of molecules in the solution is increased, each molecule of ammonia added increasing the molecular lowering by about 19.5 units (theory 18.6). The addition of 4 molecules of ammonia to a solution containing 1 molecule of copper nitrate increases the number of molecules only to a very slight extent (increase of molecular lowering 2.5), but the similar addition to a solution of copper sulphate causes an appreciable change (7.7 in the molecular lowering).\*

Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 910; *Abstr.*, 1900, ii, 265) determined the partial pressure of ammonia of ammoniacal salt solutions by drawing a current of air through the solutions contained in a thermostat at 60° into a standard acid solution. He finds that the partial pressure of the ammonia of the salt solution is expressed by the formula  $P = P_1(n - km)$ , where  $P_1$  = partial pressure of ammonia from pure aqueous ammonia solution,  $n$  = number of gram-molecules of ammonia and  $m$  = number of gram-mols. of salt per litre, and  $k$  a constant. For silver nitrate, he finds  $k = 2$ , and for cadmium nitrate, zinc nitrate, nickel chloride, copper nitrate, copper chloride, copper sulphate, and copper acetate  $k$  = approx. 4 (3.4 to

\* The effect produced by the addition of more ammonia than 4 molecules per molecule of copper salt has not been investigated, and in consequence the deduction of conclusions from Reyehler's experiments is made somewhat difficult.

4.04). Some salt solutions which are not at first precipitated by ammonia were also investigated, and it was found that the partial pressure of ammonia in such ammoniacal salt solutions was greater than the partial pressure of pure aqueous ammonia solution, except in the cases of calcium and strontium chlorides. In these two cases, there is probably some specific action between the ammonia and the dissolved electrolyte, but for the others the results are in accordance with those obtained for the influence of dissolved salts on the absorption coefficient of such gases as hydrogen, nitrogen (Steiner, *Ann. Phys. Chem.*, 1894, [ii], 52, 275; Braun, *Zeit. physikal. Chem.*, 1900, 33, 721), and nitrous oxide (Gordon, *Zeit. physikal. Chem.*, 1900, 18, 7; Roth, *Zeit. physikal. Chem.*, 1897, 24, 114), and also on the solubility of ethyl acetate (Euler, *Zeit. physikal. Chem.*, 1900, 31, 360) and phenylthiocarbamide (Rothmund, *Zeit. physikal. Chem.*, 1900, 33, 402).

According to the law of distribution (Nernst) of a substance between two non-miscible media, the condition of equilibrium at a given temperature is determined by a constant ratio of the concentrations, if the molecular weight of the distributed substance is the same in the two media. If we invert this distribution theorem, it follows that deviations from the constant concentration ratio will serve as a measure of any molecular change which the distributing substance undergoes in one or other of the media, as Hantzsch and Sebaldt (*Zeit. physikal. Chem.*, 1899, 30, 258) have pointed out. Such molecular changes probably occur in ammoniacal salt solutions, and the investigation of the distribution-coefficient of ammonia between such salt solutions and a medium non-miscible with water will indicate the formation of any complex compounds produced by combination of the salt and ammonia. The deviation of the distribution-coefficient for the salt solution from the value found for pure water and a non-miscible medium will measure the complexity of such compounds. The investigation of this deviation forms the subject of the present paper.

Hantzsch and Sebaldt (*loc. cit.*, 266), in an attempt to elucidate the constitution of ammonia and amine solutions, have investigated the distribution of these substances between water and various non-miscible organic liquids. They find that the ratio of the concentration of ammonia in water to that in chloroform is independent of the

absolute value of the concentrations, that is,  $\frac{c_1}{c_2} = \text{constant}$ , where  $c_1 =$  concentration in water, and  $c_2 =$  concentration in chloroform. In their calculations, Hantzsch and Sebaldt take account of the electrolytic dissociation of aqueous ammonia solution, but neglecting this—which is

extremely small at the concentrations used—the ratio  $\frac{c_1}{c_2}$  is practically constant. Without entering into a discussion of the nature of aqueous



ammonia solution, we can conclude from the constancy of this ratio that the molecular complexity of the ammonia in both solvents is the same. This being the case, the conditions under which the problem to be solved has been investigated are as simple as possible.

By reason of the considerable solubility of ammonia in chloroform, and, at the same time, of the small reciprocal solubility of water and chloroform, the latter is particularly adapted for our investigation.\*

#### EXPERIMENTAL.

The method of experimentation was as follows: 50 c.c. of solution containing the salt and ammonia were thoroughly shaken in a separating funnel with a known volume of chloroform. The separating funnel was placed in a thermostat, and after having acquired the temperature of the bath, the chloroform and aqueous solution were repeatedly shaken until it could be assumed that equilibrium had been established. Hantzsch and Sebaldt have shown that this takes place very quickly. After the chloroform had completely settled from the salt solution (about  $\frac{1}{2}$  hour), the funnel was removed from the thermostat, the two layers at once separated, and without any loss of time the ammonia in each was estimated. We may assume, from the result of special experiments, that during the course of the experiment practically no ammonia is lost. The amount of ammonia in the chloroform solution was determined by adding a known volume of this (either 40 or 70 c.c.) to about 80 c.c. of water contained in a stoppered bottle. This was then directly titrated with 0.1 normal acid, using methyl-orange as indicator, the end point being taken when a permanent pinkish colour appeared in the aqueous layer after shaking the chloroform through it. We have proved by preliminary experiments that this method of determining the ammonia in chloroform is accurate. In the first experiments with copper sulphate solution, the quantity of ammonia in the aqueous solution was determined by distilling a known volume of the solution, to which an excess of alkali had been added, into a known volume of normal sulphuric acid solution and titrating back, after diluting, with 0.1 normal alkali. It was also proved that the accuracy of this method is satisfactory. Besides, as we always knew the total amount of ammonia present and the volume of both the aqueous solution and the chloroform, we had a check on the analysis. In the case of colourless solutions (aqueous), it was unnecessary to distil off the ammonia, and the quantity was determined by direct titration of a

\* According to Herz (*Ber.*, 1898, 31, 2869), 100 volumes of chloroform dissolve 0.152 volume of water, and 100 volumes of water dissolve 0.420 volume of chloroform at the ordinary temperature.

known volume with 0.1 normal acid. It was afterwards found possible to titrate the copper salt solution directly, as the intense blue colour of the copper-ammonia ions disappears before the end point is reached, and the colour due to the copper ions in the very dilute solution which we used in the titration was much too weak to mask the end point in any way. The amount of ammonia found by these methods agreed perfectly. The total amount of ammonia found was usually a trifle less than that added, but the difference was nearly always less than 1 per cent. of the total, and never exceeded 1.5 per cent.

The aqueous solution was obtained by taking a known volume ( $a$ ) of normal salt solution, adding a known volume ( $b$ ) of approximately normal aqueous ammonia solution (sufficient to precipitate the metal hydroxide completely, then wholly redissolve it) and then  $(50 - a - b)$  c.c. of water. The amount of chloroform used was either 100 c.c., 70 of which were taken for the titration, or 50 c.c., of which 40 were taken. The amount of 0.1 normal acid used in the titration varied between 4 and 16 c.c. for the chloroform, and between 10 and 40 c.c. for the aqueous solution.

*Distribution-coefficient of Ammonia between Water and Chloroform.*

The results obtained at 20° with varying absolute concentrations of ammonia are given in the following table :

Total ammonia in original aqueous solution. Gram-mol. per litre.	Concentration of ammonia in $\text{CHCl}_3$ . $c_2$ . Gram per litre.	Concentration of ammonia in aqueous part. $c_1$ . Grams per litre.	Coefficient $\frac{c_1}{c_2}$	Mean.
0.365	0.2317	6.001	26.0	26.3
0.373	0.2281	6.138	26.9	
0.444	0.2730	7.295	26.7	
0.532	0.3499	8.737	26.1	
0.548	0.3380	9.024	26.7	
0.712	0.4342	11.290	26.0	
0.892	0.5431	14.140	26.0	

The deviations from the mean value shown by the above numbers are quite irregular, and no regular variation of the distribution-coefficient with the concentration is observable. The accuracy of the later determinations in the paper (after some experience had been gained) is probably much greater than that measured by the deviations of the single observations in the above series from the mean.

The coefficient decreases with rise of temperature. Thus, at 25° the results were obtained :

Total ammonia in original aqueous solution. Gram-mol. per litre.	Concentration of ammonia in chloroform. $c_2$ . Gram per litre.	Concentration of ammonia in aqueous part. $c_1$ . Grams per litre.	Coefficient, $\frac{c_1}{c_2}$	Mean.
0.286	0.1870	4.695	25.1	24.9
0.381	0.2511	6.247	24.9	
0.567	0.3111	7.667	24.7	

and at 30°:

0.382	0.2687	6.245	23.2	23.2
0.478	0.3375	7.815	23.2	

*Experiments with Copper Sulphate Solution.*

The requisite volume of normal copper sulphate solution was introduced into the separating funnel, and varying volumes of approximately normal ammonia solution added; then a volume of water so as to make the total addition up to 50 c.c. The distribution-coefficient was determined at 20° with the following results:

Total ammonia in the original solution. Gram-mol. per litre.	Concentration in $\text{CHCl}_3$ . $c_2$ . Gram per litre.	Concentration in the aqueous part. $c_1$ . Grams per litre.	Coefficient. $\frac{c_1}{c_2}$
With 0.1 normal:			
0.2403	0.0470	3.975	84.5
0.2765	0.0633	4.593	72.5
0.2814	0.0662	4.739*	71.5
0.3497	0.1129	5.858*	51.9
0.3635	0.1152	5.974	51.9
0.4473	0.1618	7.474*	46.2
0.4564	0.1675	7.456	44.5
0.5374	0.2141	8.746	40.9
0.5608	0.2314	9.840*	40.4
0.6286	0.2668	10.465*	39.3
0.6887	0.2679	10.220	38.2
0.7201	0.3228	11.680	36.2
0.8047	0.3779	12.980	34.3
With 0.4 normal:			
0.9256	0.1148	15.500	135.1
1.2302	0.2961	20.420	69.0
1.5396	0.4906	25.300	51.6

\* The ammonia was determined by distillation; in the other cases by direct titration. In the cases marked with an asterisk also 50 c.c. of chloroform were used, and 40 taken for the titration, otherwise 100 were used and 70 taken.

Total ammonia in the original solution. Gram-mol. per litre.	Concentration in $\text{CHCl}_3$ . $c_2$ . Gram per litre.	Concentration in the aqueous part. $c_1$ . Grams per litre.	Coefficient. $\frac{c_1}{c_2}$
With 0.2 normal :			
0.4590	0.0700	7.695	109.3
0.5509	0.1168	9.170	78.5
0.6408	0.1708	10.590	62.2
0.7338	0.2225	12.080	54.3
0.9165	0.3316	14.980	45.2
With 0.05 normal :			
0.1741	0.0566	2.915	51.5
0.2681	0.1084	4.359	40.2
0.3564	0.1587	5.780	36.4
0.8575	0.1610	5.942	36.9

Ten c.c. of approximately normal ammonia solution were not sufficient to precipitate and completely redissolve the copper salt in 5 c.c. of normal copper sulphate solution, so that we may safely assume that it requires more than 4 molecules of ammonia per molecule of copper sulphate to transform the whole of the copper salt into the complex compound and at the same time leave no undissolved residue.

Conclusions as to the nature of the compound formed are drawn later in the paper—at present we may notice that the above results are included in the curves given on p. 1251.

These results show that the concentration of ammonia in the chloroform depends, not only on the amount of ammonia, but also on the concentration of the salt in the aqueous solution.

The coefficient thus obtained gives the ratio of the concentration of the total ammonia in the aqueous part to that in the chloroform. If we assume that the salt solution would give the same coefficient as pure water provided that no action took place between the salt and ammonia, then from the knowledge of the distribution-coefficient between pure water and chloroform, we may calculate from the concentration in the chloroform the concentration of ammonia in the salt solution which is necessary in order that equilibrium may exist between the dissolved ammonia in the two media. This latter we may regard as free ammonia and the difference from the total ammonia will give us the fixed ammonia, and knowing the concentration of the salt solution we may further calculate the molecular ratio between fixed ammonia and salt.

Since a possible experimental error of 0.5 unit may be made in the determination of the distribution-coefficients, we have considered it best to plot mean curves with the concentration of ammonia in chloroform as abscissa and distribution-coefficient as ordinate, and

from these curves to calculate the proportion of fixed ammonia at any concentration, rather than from each separate experiment.

Before the results obtained from these curves are given, we proceed to show that the same curves are capable of representing the experimental results arrived at with other salts than copper sulphate.

#### *Experiments with Copper Chloride.*

A normal solution of this salt was prepared by precipitating a solution of 12.488 grams of crystallised copper sulphate with hot caustic potash, filtering and washing the copper oxide, and dissolving it in hydrochloric acid. The copper chloride solution was evaporated to dryness, then dissolved in water and evaporated again to dryness, and this was repeated until the residue showed scarcely any acid reaction. It was then dissolved in water and made up to 100 c.c. The solution so obtained was acid, but it was proved that the error introduced on account of ammonia required to neutralise this was negligibly small.

The distribution-coefficient was determined in a tenth normal solution at 20° with varying concentration of ammonia with the following results :

Total $\text{NH}_3$ in original solution. Gram-mol. per litre.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ . Gram per litre.	Concentration of $\text{NH}_3$ in aqueous part. Grams per litre.	Coefficient.
0.2808	0.0662	4.729	71.4
0.4682	0.1719	7.821	45.5
0.6581	0.2884	10.947	38.0

If we compare these coefficients with those obtained in decinormal copper sulphate solution at corresponding concentrations of ammonia, we find that they agree closely and certainly within the experimental error.

#### *Experiments with Zinc Sulphate.*

A normal solution of zinc sulphate was prepared by dissolving 14 grams of the crystallised salt  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in water and making up the solution to 100 c.c. To the requisite volume of this solution with varying quantities of approximately normal ammonia, water was added so as to make the total addition up to 50 c.c. and the coefficient was determined with this, when the following results were obtained :

Total $\text{NH}_3$ in original solution. Gram-mol. per litre.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ . Gram per litre.	Concentration of $\text{NH}_3$ in aqueous part. Grams per litre.	Coefficient.
With 0.1 normal :			
0.4689	0.1727	7.832	45.2
0.5449	0.2204	8.861	40.2
0.5611	0.2306	9.349	40.5
0.6613	0.2876	11.001	38.2
With 0.05 normal :			
0.3740	0.1714	6.213	36.4
0.4634	0.2260	7.684	34.0
0.5358	0.2679	8.610	32.2
0.5650	0.2868	9.357	32.6
0.6295	0.3230	10.100	31.3
0.6613	0.3455	10.888	31.5
With 0.025 normal :			
0.3752	0.2021	6.205	30.7
0.4675	0.2591	7.722	29.8
0.5593	0.3165	9.232	29.2

With decinormal and twentieth normal copper sulphate solutions and the same concentration of ammonia, almost the same coefficients were obtained.

#### *Experiments with Cadmium Iodide.*

A normal solution was prepared by dissolving 18.3 grams of cadmium iodide in water and making up to 100 c.c.

As the cadmium hydroxide precipitated by the ammonia is not so easily redissolved, only a single experiment was made in decinormal solution, using 5 c.c. of the above solution, 40 c.c. of normal ammonia and 5 c.c. of water. The result obtained agrees closely with that found with decinormal copper sulphate solution, and similar absolute concentration of ammonia.

With twentieth normal cadmium iodide solution, the smallest amount of ammonia which would completely precipitate and redissolve 5 c.c. of semi-normal cadmium iodide solution was between 25 and 30 c.c. of normal ammonia solution. An experiment was made with 25 c.c. of normal ammonia, but a decided precipitate remained in the aqueous part; with 30 c.c., however, the cadmium hydroxide was completely dissolved. We give the result of the experiment with 25 c.c. of ammonia, but do not place any reliance on the figures :

Total $\text{NH}_3$ in original solution. Gram-mol. per litre.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ . Gram per litre.	Concentration of $\text{NH}_3$ in aqueous part. Grams per litre.	Coefficient.
With 0.1 normal : 0.7642	0.3572	12.688	35.5
With 0.05 normal : 0.4789 0.5712 0.6636 0.7633	0.2402 0.2906 0.3490 0.4167	7.935 9.458 10.979 12.642	33.0 32.5 31.5 30.8

Experiments have also been made with tenth, twentieth, and fortieth normal nickel sulphate solutions, but the separated hydroxide requires the addition of considerable quantities of ammonia before a clear solution is obtained. Without giving the actual results, we may say that they are substantially the same as those obtained with similar concentrations of copper and zinc sulphates.

In order to ascertain whether an increase in the concentration of the  $\text{SO}_4$  ions in the copper sulphate solution had any influence on the distribution-coefficient, experiments were made with solutions containing a fixed quantity of copper sulphate and (1) varying quantities of sodium sulphate and a fixed amount of ammonia, and (2) varying quantities of ammonia and a fixed amount of sodium sulphate. In the first place, however, the influence of sodium sulphate alone on the distribution-coefficient was determined and it was found that even with fairly large quantities of sodium sulphate the coefficient was but slightly altered, as the following results show. The same quantity of ammonia was added in each case and for comparison the mean value obtained for pure water is appended :

Concentration of $\text{Na}_2\text{SO}_4$ in aqueous part. Gram equivalent per litre.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ . Gram per litre.	Concentration of $\text{NH}_3$ in aqueous part. Grams per litre.	Coefficient.
0.4	0.2979	7.233	24.3
0.2	0.2885	7.199	25.0
0.1	0.2836	7.240	25.5
0.0	—	—	26.3

The distribution-coefficient obviously decreases gradually as the concentration of the sodium salt increases, which would indicate a

decrease of the solubility of ammonia in the aqueous solution with increasing concentration of sodium sulphate.

From the experimental material relating to the influence of dissolved electrolytes on the absorption-coefficient of water for nitrous oxide and hydrogen, Jahn (*Zeit. physikal. Chem.*, 1895, 18, 8) has deduced an empirical relationship which may be expressed by the equation

$$\frac{\alpha - \alpha'}{m^2} = \text{const.},$$

where  $\alpha$  is the absorption coefficient of pure water,  $\alpha'$  that of the solution, and  $m$  the concentration of the dissolved salt in gram-mol. per litre. Although the above values for the distribution-coefficient do not differ much from one another, yet in consideration of the quantities of decinormal acid used in the titrations (12 c.c. for the chloroform, 22 c.c. for the aqueous solution), the numbers are probably accurate to 0.5 per cent. It seemed desirable, therefore, to test whether this empirical equation is capable of representing the dependence of the distribution-coefficient of ammonia on the concentration of the sodium sulphate in the solution.

For the three solutions, the following values are obtained :

Conc. of $\text{Na}_2\text{SO}_4$ .	$m=0.05$ .	$m=0.1$ .	$m=0.2$ .
$\frac{\alpha - \alpha'}{m^2}$	$=5.8$	6.0	5.9

The expression given by Jahn therefore appears to be capable of representing in this case the influence of the dissolved electrolyte on the distribution-coefficient of ammonia.\*

The following table contains the results of experiments made with decinormal copper sulphate solutions, the concentration of the sodium sulphate in the solution varying from 0.1 to 0.4 normal, whilst the amount of ammonia added was the same throughout :

Concentration of $\text{Na}_2\text{SO}_4$ in aqueous part. Gram equivalent per litre.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ . Gram per litre.	Concentration of $\text{NH}_3$ in aqueous part. Grams per litre.	Coefficient.
0	0.1675	7.456	44.5
0.1	0.1718	7.437	43.3
0.2	0.1766	7.440	42.1
0.3	0.1792	7.444	41.5
0.4	0.1815	7.447	41.0

We are at present engaged in carrying out further experiments with a view of determining the influence of dissolved substances on the distribution-coefficient of ammonia between solutions and chloroform.



The presence of considerable quantities of sodium sulphate has, therefore, very little effect on the ratio of distribution of ammonia between the copper sulphate solution and chloroform. The variation is of the same order of magnitude as was obtained in the case of solutions containing no copper sulphate, as is evident from the following comparison :

	$\frac{c_1}{c_2}$	Diminution of $\frac{c_1}{c_2}$ .
Water .....	26.3	} 7.6 per cent.
0.4 normal $\text{Na}_2\text{SO}_4$ solution .....	24.3	
0.1 normal $\text{CuSO}_4$ solution .....	44.5	} 7.8 "
0.1 normal $\text{CuSO}_4$ + 0.4 normal $\text{Na}_2\text{SO}_4$ sol. ....	41.0	

A similar small influence of the sodium sulphate is observable if the concentration of the ammonia is varied as the following table indicates, the corresponding values for the same concentrations of ammonia without sodium sulphate being added for comparison :

With 0.1 normal  $\text{CuSO}_4$  and 0.4 normal  $\text{Na}_2\text{SO}_4$  :

Concentration of $\text{NH}_3$ in original solution. Gram-mol. per litre.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ . Gram per litre.	Concentration of $\text{NH}_3$ in aqueous part. Grams per litre.	Coefficient.	Coefficient without $\text{Na}_2\text{SO}_4$ .
0.2774	0.0675	4.582	67.9	69.8
0.3678	0.1243	6.003	48.2	50.2
0.4594	0.1815	7.447	41.0	42.5

From these data, it is evident that the only influence exerted by the sodium sulphate on the distribution of ammonia between copper sulphate solution and chloroform is of the same nature and magnitude as the influence exerted on the distribution equilibrium between water and chloroform. The sodium sulphate exerts apparently no specific action on the copper salt as regards the formation of the complex ammonia compound, although in the above solutions of the mixed sulphates the degree of dissociation of the copper sulphate is diminished to a very considerable extent. The action of sodium sulphate on the ratio of the free and combined ammonia in the copper salt solution will be referred to later.

Two or three determinations were also carried out at  $20^\circ$  with calcium chloride solutions. Whereas the presence of sodium sulphate produces an effect such that for a given concentration of ammonia in the chloroform the concentration in the aqueous solution as compared with that in pure water is diminished, the calcium chloride acts in the opposite direction, and must be classed with the salts of copper, cadmium, zinc, and nickel. This corresponds with the results arrived

at by Konowaloff for the partial pressure of ammonia over solutions of calcium chloride.

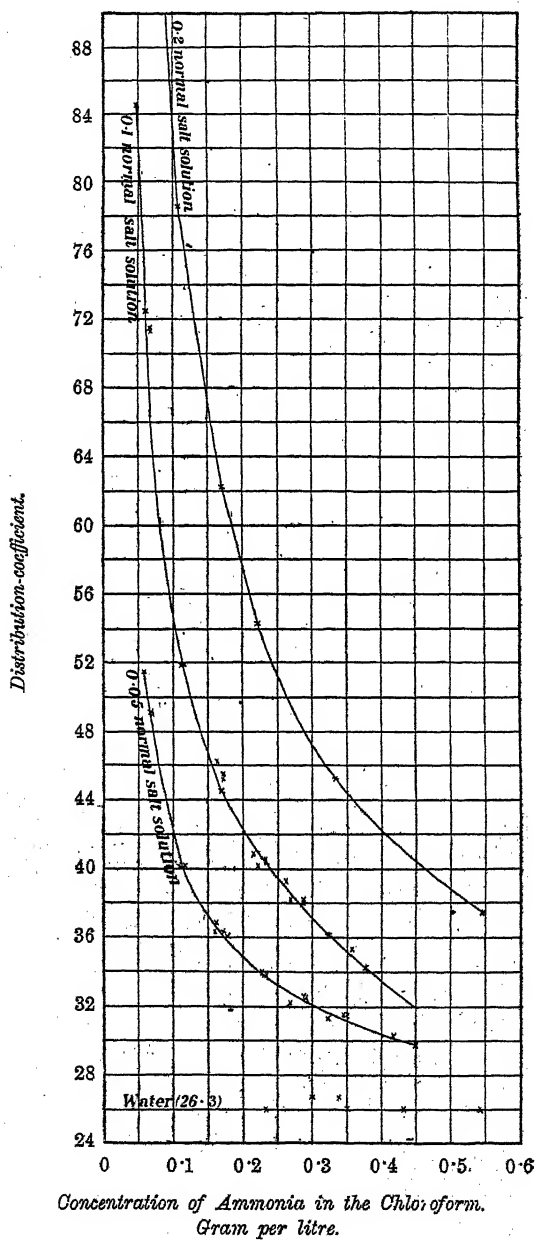
The following numbers were obtained:

Concentration of $\text{NH}_3$ in original solution. Gram-mol. per litre.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ . Gram per litre.	Concentration of $\text{NH}_3$ in aqueous part. Grams per litre.	Coefficient.
With 0.2 normal calcium chloride solution:			
0.3640	0.2125	6.002	28.2
With 0.1 normal calcium chloride solution:			
0.2652	0.1585	4.369	27.6
0.4384	0.2645	7.220	27.3

If the value of the distribution-coefficient obtained in the first experiment be compared with that found with a copper sulphate solution of the same strength and with the same concentration of ammonia in the chloroform layer, an enormous difference is observable, the two numbers being 56 and 28.2. The amount of ammonia fixed by the calcium chloride is, therefore, very small, and if it be assumed that an ammonia complex of the same type as that yielded by copper, zinc, and cadmium is formed, the calcium-ammonia compound must be dissociated to a relatively far greater extent than the other compounds.

With the results obtained above, mean curves have been drawn, showing the dependence of the distribution-coefficient on the concentration of the ammonia in the chloroform layer. It has been found that one curve will represent the 0.1 normal solutions of copper sulphate, zinc sulphate, copper chloride, and cadmium iodide, and that another curve will represent exactly the results for 0.05 normal solutions of copper sulphate, zinc sulphate, and cadmium iodide. These curves are shown in the figure on p. 1251. The curve is a mean one, and in the calculation of the amount of fixed ammonia, none of the experimental results were used directly. For the purpose of calculation, we have selected points on the curve representing ammonia concentrations corresponding with a certain integral number of molecules of ammonia per molecule of salt in the aqueous solution after the distribution had taken place. Thus, in a decinormal solution of any of the salts used, the concentration of the salt was 0.05 molecule per litre, and the concentrations of the ammonia chosen were respectively 0.25, 0.30, 0.35, 0.40, 0.45, and 0.50 molecule, or 5.975, 6.828, 7.681, 8.535 grams, per litre, that is, the

*Variation of distribution-coefficient with varying concentration of the Ammonia.*



ratio of salt molecules to ammonia molecules was 1:5, 1:6, 1:7, 1:8, 1:9, 1:10. Now, the concentration of ammonia in the aqueous solution is not given by the curve; we had, therefore, to ascertain by trial the points on the curve corresponding to the special concentrations required, the coefficient multiplied by the concentration in chloroform giving the concentration of ammonia in the aqueous solution. It is obvious that only a part of the curve is of use for calculating accurately the fixed ammonia. If the coefficient is too small and near the coefficient for pure water (26.3), then, since the difference of these two numbers is a factor in the calculation, the error becomes considerable; on the other hand, when the coefficient is too high, this means that the concentration of ammonia in the chloroform is too small to permit of its being determined with any great degree of accuracy. In our calculations of the fixed ammonia, we have remained within such limits that the experimental errors do not vitiate our conclusions.

In the following tables, the last column contains the ratio of the number of molecules of 'fixed' ammonia per molecule of salt, the second column the ratio of the total number of molecules of ammonia per salt molecule.

Strength of $\text{NH}_3$ in aqueous part.	Mol. ratio of salt: total $\text{NH}_3$ in aqueous part.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ Gram per litre.	Co-efficient.	Free $\text{NH}_3$ Grams per litre.	Fixed $\text{NH}_3$ Grams per litre.	Fixed $\text{NH}_3$ Gram-mol. per litre.	Mol. ratio. Salt: $\text{NH}_3$ .
With 0.1 normal solutions:							
0.25 N	1: 5	0.06	71	4.260	2.682	0.157	1: 3.14
0.30	1: 6	0.09	57	5.130	2.763	0.162	1: 3.24
0.35	1: 7	0.1175	51.2	6.015	2.926	0.171	1: 3.43
0.40	1: 8	0.145	47	6.815	3.002	0.176	1: 3.52
0.45	1: 9	0.175	44	7.700	3.098	0.181	1: 3.63
0.50	1: 10	0.205	42	8.610	3.208	0.188	1: 3.76
With 0.05 normal solutions:							
0.15 N	1: 6	0.0475	54.6	2.593	1.344	0.079	1: 3.16
0.175	1: 7	0.0575	51.7	2.973	1.460	0.086	1: 3.44
0.20	1: 8	0.0725	47.7	3.458	1.551	0.091	1: 3.64
0.225	1: 9	0.085	45.0	3.825	1.589	0.093	1: 3.72
0.25	1: 10	0.1025	41.7	4.274	1.578	0.092	1: 3.68
0.30	1: 12	0.1350	38.1	5.143	1.598	0.093	1: 3.72
0.35	1: 14	0.1650	36.4	6.006	1.665	0.097	1: 3.88
0.40	1: 16	0.1925	35.1	6.757	1.694	0.099	1: 3.96
0.45	1: 18	0.225	34.0	7.650	1.732	0.101	1: 4.04

For completeness, the same tabulation is given for the stronger solutions of copper sulphate, which have been used, the proportions of fixed ammonia per molecule of salt being calculated in this case directly from the concentrations of ammonia actually employed in the experiments—the number of observations not being sufficient for tracing a curve.

Mol. ratio of salt to total $\text{NH}_3$ .	Free $\text{NH}_3$ . Grams per litre.	Fixed $\text{NH}_3$ . Grams per litre.	Fixed $\text{NH}_3$ . Gram-mol. per litre.	Mol. ratio. Salt : fixed $\text{NH}_3$ .
With 0.2 normal copper sulphate :				
1 : 4.51	1.842	5.853	0.343	1 : 3.43
1 : 5.37	3.072	6.098	0.357	1 : 3.57
1 : 6.20	4.479	6.111	0.358	1 : 3.58
1 : 7.08	5.852	6.228	0.365	1 : 3.65
With 0.4 normal copper sulphate :				
1 : 4.54	3.019	12.48	0.731	1 : 3.65
1 : 5.38	7.787	12.63	0.740	1 : 3.70
1 : 7.41	12.900	12.40	0.727	1 : 3.64

At all concentrations investigated, the amount of ammonia combined with 1 molecule of salt slowly increases as the total concentration of the ammonia becomes larger. This increase in the amount of fixed ammonia is, however, relatively small, for example, in the case of decinormal copper sulphate solution, the further addition of a quantity of ammonia equal to that sufficient to conveniently dissolve the originally precipitated hydroxide (100 per cent. increase in total ammonia) only produces an increase of about 11 per cent. in the former. Furthermore, it appears that with increasing concentration of the copper sulphate solution the effect of doubling the total amount of ammonia under the same conditions is less, that is, the relative increase of the fixed ammonia becomes smaller.

Another comparison which enables us to get a fuller insight into the nature of the equilibrium in the ammoniacal salt solution is that of the amount of combined ammonia for the same molecular ratio between the salt and the total ammonia at different dilutions. The proportion 6 molecules of total ammonia per molecule of salt lies within the range of the experiments at all the concentrations of copper sulphate investigated, and for this reason has been chosen for the comparison :

Mol. ratio of $\text{CuSO}_4$ to total $\text{NH}_3$ .	Concentration of $\text{CuSO}_4$ .	Mol. ratio of $\text{CuSO}_4$ to fixed $\text{NH}_3$ .
1:6	0.05 <i>N</i>	1:3.16
1:6	0.1	1:3.24
1:6	0.2	1:3.58
1:6	0.4	1:3.70

Dilution of the solution is obviously accompanied by an increase in the dissociation of the copper ammonia compound, its influence being opposite to that due to an increase in the proportion of ammonia relatively to the copper salt. Further dilution is attended by precipitation, indicating that as the above dissociation increases the solution becomes saturated with regard to one of the dissociation products. It is further of interest to calculate in the same way the amount of fixed ammonia per molecule of salt for the same molecular ratio between the total ammonia and copper salt in presence of varying quantities of sodium sulphate. In the calculation of the free ammonia in the aqueous solution, it is obviously incorrect to use the value of the distribution coefficient for pure water and chloroform, and the value of the coefficient obtained on p. 1247 for the corresponding pure sodium sulphate solution has been employed.

With 0.1 normal copper sulphate solution :

Concentration of $\text{Na}_2\text{SO}_4$ .	Coefficient.	Free $\text{NH}_3$ . Grams per litre.	Fixed $\text{NH}_3$ . Grams per litre.	Fixed $\text{NH}_3$ . Gram-mol. per litre.	Mol. ratio of $\text{CuSO}_4$ to fixed $\text{NH}_3$ .
0 <i>N</i>	26.3	4.405	3.051	0.1787	1:3.57
0.1	25.5	4.381	3.056	0.1790	1:3.58
0.2	25.0	4.415	3.025	0.1772	1:3.54
0.3	24.6	4.408	3.036	0.1779	1:3.56
0.4	24.3	4.410	3.037	0.1779	1:3.56

At all concentrations of sodium sulphate, the proportion of fixed ammonia is exactly the same within the limits of experimental error, the deviation from the mean being but 0.5 per cent.

The results thus far obtained would indicate that in all the solutions investigated, in presence of a considerable excess of ammonia, 1 molecule of the salt takes up 4 molecules of ammonia in some way or another, so that the latter can no longer act as free ammonia and participate directly in the equilibrium which is established between the salt and the ammonia in the chloroform. As the amount of ammonia

decreases with reference to the amount of salt, or if the ratio of these remains constant and the dilution increases, the compound formed in solution gradually undergoes dissociation so that the combined ammonia per molecule of salt is considerably diminished, the lowest ratio obtained in our experiments being 3.16 molecules of ammonia per molecule of salt. The assumption of a dissociating compound,  $\text{CuSO}_4 \cdot 4\text{NH}_3$ , would agree with this, and with the fact that on addition of alcohol to an ammoniacal copper sulphate solution a compound of the formula  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$  is precipitated, although the latter observation does not prove that this compound is present in considerable quantity, for the addition of alcohol may result in a disturbance of the conditions of equilibrium, and in the resulting alcoholic solution the solubility product of the above compound may be small. If we assume, however (as is generally done), that the above compound dissociates electrolytically with the formation of  $\text{Cu}^{2+}$  and  $4\text{NH}_3$  and  $\text{SO}_4$  ions, then whether the ammonia in solution is a dissociation product of the undissociated salt or of the positive ion, we should expect to find that the addition of sodium sulphate would have some influence on the equilibrium between the copper salt and the ammonia, for application of the law of mass action shows that the concentration of the positive ion as well as that of the undissociated complex will be altered as a result of the increase in concentration of the  $\text{SO}_4$  ions. Experiment shows, however, that the addition of sodium sulphate has no influence on the equilibrium in question, the proportion of combined ammonia at the same concentration being the same.

Results which we have obtained with ammoniacal solutions of copper oxide seem to indicate that such a complex can not be exclusively formed in the salt solutions. The blue colour of the solution of copper oxide in ammonia is apparently the same as that of a solution obtained by precipitating a cold solution of a copper salt with ammonia and redissolving in excess, and we should consequently expect that the same complex would be present.

Although in the case of the oxide more ammonia is required to obtain a clear solution containing a given quantity of copper than in the case of the salts, the amount of combined ammonia referred to one atom of copper is, however, very much smaller in the former case, as will be seen from the succeeding details.

#### *Experiments with Copper Oxide.*

Some copper sulphate was precipitated with alkali and well washed by decantation. The copper oxide was then shaken with ammonia solution (approximately normal). The amount of copper oxide in the solution was determined by evaporating a known volume to dryness,

igniting, and weighing the residual copper oxide. 140 c.c. gave 0.2236 gram CuO, that is, the solution was 0.0401 normal.

Fifty c.c. of this solution were shaken with 100 c.c. of chloroform, and the distribution-coefficient determined, result A being obtained :

Total $\text{NH}_3$ in original solution. Gram-mol. per litre.	Concentration of $\text{NH}_3$ in $\text{CHCl}_3$ . Gram per litre.	Concentration of $\text{NH}_3$ in aqueous part. Grams per litre.	Coefficient
A. 0.7278 B. 0.1734	0.4477 0.03979	12.200 1.440	27.25 36.2

Calculating from the concentration of ammonia in the chloroform that the concentration of free ammonia in the aqueous part is  $0.4477 \times 26.3 = 11.774$  grams per litre, this leaves  $12.2 - 11.774 = 0.426$  gram per litre of ammonia in combination with the copper oxide. That is, 0.0201 gram-mol. of copper oxide is combined with 0.0249 gram-mol. of ammonia ; the complexity is represented by  $\text{CuO}, 1.24\text{NH}_3$ .

A current of air, free from carbon dioxide, was aspirated through 100 c.c. of the ammoniacal copper oxide solution ; the ammonia was absorbed by a measured volume of sulphuric acid as a gauge of the amount of ammonia lost. After sufficient ammonia had been removed, so that a higher coefficient would be obtained, the solution was made up to 100 c.c., the concentration of copper thus remaining the same. A very slight turbidity was produced on addition of the small quantity of water. The distribution coefficient was determined with this solution, and the result B (above) obtained. Calculating as before, we have

Free ammonia in aq. part,  $0.03979 \times 26.3 = 1.046$  ;

Fixed ammonia,  $1.440 - 1.046 = 0.394$  gram per litre,

or 0.0231 gram-mol. per litre.

Therefore,  $0.02\text{CuO} : 0.0231\text{NH}_3$ ,

that is, the complexity is represented by  $\text{CuO}, 1.15\text{NH}_3$ .

Two portions of the original ammoniacal solution were again treated as above, but instead of making up to 100 c.c. with water, dilute ammonia was added, and thus any slight formation of a precipitate was avoided.

With these solutions and two others prepared in the same way, which were respectively 0.0225 and 0.08 normal with respect to the dissolved copper oxide, the distribution coefficients were determined before. All the results are contained in the following table, with exception of the first experiment, which is omitted in consequence



of the use of a large excess of ammonia. With regard to the most concentrated copper oxide solution (0.08 normal), it should be mentioned that this was obtained as the result of an attempt to prepare as strong a solution as possible. For this purpose, ordinary copper oxide, which appears to dissolve somewhat more readily than the precipitated oxide, was shaken with fairly strong ammonia (4 normal) for a considerable time, and after filtering through asbestos exposed to a current of air as before until a precipitate began to be formed. The solution was again filtered, the amount of dissolved copper oxide estimated, and a portion used at once for the determination of the distribution-coefficient. A further precipitation was observed to have taken place from the solution after standing 24 hours, although the number of molecules of ammonia per molecule of copper oxide in the solution was about 7. A solution containing the same amount of copper present as sulphate, on the other hand, has no tendency to precipitate if 5 molecules (or even less) of ammonia are present.

Mols. total NH <sub>3</sub> per mol. of CuO in original solution.	Concentra- tion of NH <sub>3</sub> in CHCl <sub>3</sub> , Gram per litre.	Concentra- tion of NH <sub>3</sub> in aqueous part, Grams per litre.	Coefficient.	Fixed NH <sub>3</sub> , Gram per litre.	Fixed NH <sub>3</sub> , Gram-mol. per litre.	Mol. fixed NH <sub>3</sub> per mol. of CuO.
With 0.04 normal copper oxide :						
9.17	0.0996	3.131	31.4	0.512	0.030	1.50
6.07	0.0612	2.073	33.9	0.464	0.0272	1.36
4.22	0.03979	1.440	36.2	0.394	0.0231	1.15
With 0.0225 normal copper oxide :						
24.2	0.1627	4.642	28.55	0.363	0.0212	1.89
With 0.08 normal copper oxide :						
6.90	0.1439	4.717	32.8	0.933	0.0547	1.37

Although the experimental errors in these determinations are greater than in the case of the salts, it is evident that we have to deal here, as before, with a dissociation phenomenon. The series of experiments with 0.04 normal copper oxide solutions shows that, by increasing the concentration of the ammonia, the concentration of the complex copper-ammonia compound is also increased, and the experiment with 0.0225 normal copper oxide shows that in presence of a

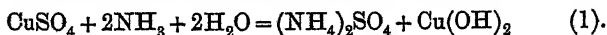
large excess of ammonia the number of molecules of ammonia combined per molecule of copper oxide approximates to two. The effect of dilution on the proportion of fixed ammonia (the ratio of total ammonia to copper oxide remaining constant) cannot be deduced from the above numbers, very probably on account of the unavoidable errors of experiment. This would, however, appear to be the same as in the case of the salt solutions, for dilution leads eventually to precipitation in each instance.

We may say that the experimental data point to the formation of a dissociating compound of the formula  $\text{CuO} \cdot 2\text{NH}_3$  or  $\text{Cu} \cdot 2\text{NH}_3 \cdot (\text{OH})_2$ , which compound is a di-acid base dissociating electrolytically with formation of  $\text{Cu} \cdot 2\text{NH}_3$  and  $\text{OH}$  ions. Whether the ammonia is a dissociation product of the positive ion or of the undissociated compound cannot as yet be definitely answered.

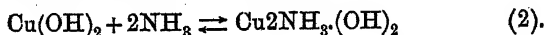
If we now turn again to the consideration of the equilibrium in ammoniacal solutions of copper salts, some light may be thrown on the nature of this from the results obtained with copper oxide solutions. The deep blue colour of the solutions appears to be the same, dilution of each solution leads apparently to the precipitation of copper hydroxide, and in each case we have a dissociation phenomenon in which ammonia is one of the dissociation products, the only difference being that whereas in presence of a large excess of ammonia 2 molecules of ammonia become fixed per molecule of copper oxide, in the case of the salts for 1 molecule of the latter we have 4 molecules of ammonia combined, and further, that in the former case, for the same quantity of copper more ammonia is required for the complete solution than in the latter.

When ammonia is gradually added to a solution of a copper salt the following changes probably occur:

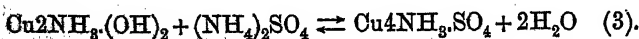
In the first stage, copper hydroxide is precipitated.



The copper hydroxide then dissolves in excess of ammonia with the formation of the soluble base  $\text{Cu} \cdot 2\text{NH}_3 \cdot (\text{OH})_2$ .



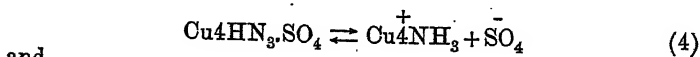
The complex base probably reacts further with the ammonium sulphate thus:



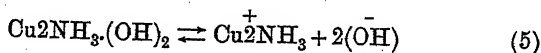
The complex salt  $\text{Cu} \cdot 4\text{NH}_3 \cdot \text{SO}_4$  and the base  $\text{Cu} \cdot 2\text{NH}_3 \cdot (\text{OH})_2$  probably exist in the ammoniacal copper salt solution. According to equation (3), the effect of dilution would be a progress of the reaction from right to left, which would, however, result in an increase of the

complex base; if equation (2) represents, however, a dissociation equilibrium, it is obvious that increasing dilution of the salt solution will lead eventually to precipitation of the copper hydroxide.

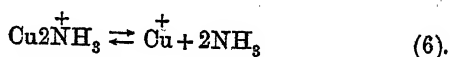
The complex cupriammonia salt and the cupriammonia base are also probably electrolytically dissociated according to



and



Increase in the concentration of the  $\text{SO}_4$  ions by the addition of sodium sulphate solution would influence the first ionic equilibrium so as to produce greater concentration of the undissociated salt, but the ammonium sulphate, which is one of the components on the other side of the equilibrium equation (3), is also influenced in the same manner, and as a consequence the addition of sodium sulphate may have but slight influence on this equilibrium. As regards the molecular species of which the ammonia is a dissociation product, we may suppose that these are the ionic complexes  $\text{Cu}_4\text{NH}_3$  and  $\text{Cu}_2\text{NH}_3$ , dissociating according to the scheme



This last equation is really nothing else than equation (2) written in ionic language, for the hydroxyl ion is common to both sides.

According to the views brought forward, increasing concentration of the ammonia in the ammoniacal copper oxide solution will result finally in the fixing of 2 molecules of ammonia per atom of copper, and in the ammoniacal copper salt solution of 4 molecules of ammonia per atom of copper.

Reychler's observation that the freezing point of copper sulphate solution is only lowered to a comparatively small extent by the addition of 4 molecules of ammonia per molecule of salt would seem to indicate that the reaction represented by equation (3) has taken place to a considerable extent from left to right with the formation of  $\text{Cu}_4\text{NH}_3\cdot\text{SO}_4$ , for only in this case can the correspondingly small increase in the number of molecules or ions in the solution be explained.

The fact that addition of alcohol to an ammoniacal copper sulphate solution results in the precipitation of  $\text{CuSO}_4\cdot 4\text{NH}_3\cdot\text{H}_2\text{O}$  is also capable of being explained on the above theory. Equation (3) also possibly explains the circumstance that, at the same concentration of copper, less ammonia per atom of copper is required for complete solution in the case of the salts than in the case of the solution free from an acid radicle.

The behaviour of the ammoniacal copper oxide and salt solutions on titration with decinormal acid should be noticed. At first deep blue, the ammoniacal copper oxide solution gradually becomes paler in colour and a precipitate is formed, the disappearance of which occurs just when the end point is reached. The acid probably reacts in the first place on the free ammonia present in the solution, converting this into ammonium ions, and diminishing in this way the product of the concentrations of the dissociation products on the left-hand side of equation (2), or (with reference to the ions) on the right-hand side of equation (6). The consequence of this is further dissociation of the complex, and attainment of the limit of solubility of copper hydroxide which is then precipitated, being afterwards dissolved by the last portions of acid. It appears probable that solutions supersaturated with regard to copper hydroxide are obtained, and that separation only takes place slowly under certain circumstances. As has been pointed out, a clear 0.08 normal solution of copper oxide containing about 7 molecules of ammonia per molecule of copper oxide gave a considerable precipitate on standing for 24 hours.

Similar phenomena are observed on titrating ammoniacal solutions of copper salts, and these can be explained in the same manner as in the case of the oxide. In both instances, the dilution resulting from the addition of the acid solution will aid in the precipitation of the copper hydroxide.

What has been said in regard to the copper sulphate solutions probably holds good for the salts of the other metals investigated: copper chloride, zinc sulphate, cadmium iodide, and nickel sulphate. It has been shown that under the same conditions, and for the concentrations used by us, the number of molecules of ammonia fixed per molecule of salt is the same in every case. The fact that increasing quantities of ammonia are required for the production of a clear solution with zinc sulphate, cadmium iodide, and nickel sulphate suggests that the dissociation of the complex formed in these solutions proceeds to a greater extent than that of the copper salt solution, but the relative solubility of the hydroxides must also be taken into account.

In the case of ammoniacal solutions of calcium chloride, the much smaller quantity of ammonia fixed at corresponding concentrations would point to a much higher degree of dissociation of the complex as compared with those of the above metal salts. The absence of any precipitation is accounted for by the much greater solubility of calcium hydroxide. It should finally be noted that the values obtained for the amount of ammonia fixed per molecule of salt agree reasonably with those obtained by Konowaloff (*loc. cit.*) from deter-

minations of the partial pressure of ammonia over ammoniacal salt solutions.

All the above experiments were carried out at 20°; we have also investigated the influence of temperature on the dissociation equilibrium in ammoniacal salt solutions.

Experiments have been made at 25° and at 30° with *zinc sulphate solutions*, and the results are tabulated below :

At 25°,  $k = 24.9$  (see page 1243):

Total NH <sub>3</sub> in original solution. Gram-mol. per litre.	Concentration of NH <sub>3</sub> in CHCl <sub>3</sub> . Gram per litre.	Concentration of NH <sub>3</sub> in aqueous part. Grams per litre.	Coefficient. $k$ .
With 0.1 normal :			
0.466	0.1878	7.761	41.2
0.657	0.3090	10.910	35.3
With 0.05 normal :			
0.468	0.2499	7.744	31.0
0.562	0.3061	9.294	29.7
0.655	0.3715	10.800	29.1
With 0.025 normal :			
0.280	0.1518	4.629	30.5
0.375	0.2138	6.181	28.9
0.469	0.2754	7.728	28.0
0.566	0.3450	9.309	26.9
0.652	0.4071	10.723	26.4
0.653	0.4046	10.746	26.6

At 30°,  $k = 23.2$  (see page 1243):

Total NH <sub>3</sub> in original solution. Gram-mol. per litre.	Concentration of NH <sub>3</sub> in CHCl <sub>3</sub> . Gram per litre.	Concentration of NH <sub>3</sub> in aqueous part. Grams per litre.	Coefficient. $k$ .
With 0.1 normal :			
0.573	0.2738	9.512	34.7
0.669	0.3375	11.088	32.3
0.765	0.4096	12.648	30.9
With 0.05 normal :			
0.384	0.2033	6.342	31.2
0.480	0.2703	7.925	29.3
0.573	0.3366	9.442	28.1
With 0.025 normal :			
0.193	0.1006	3.183	31.6
0.383	0.2339	6.309	27.0
0.575	0.3652	9.445	25.9

A comparison of the numbers obtained at these higher temperatures with those for  $20^{\circ}$  shows that the nature of the equilibrium in solution has undergone no change. The calculation of the quantity of fixed ammonia from the above experimental data shows that for 1 molecule of salt there are from 3 to 4 molecules of ammonia combined. As at  $20^{\circ}$ , also, increasing concentration of ammonia tends to make this molecular ratio approximate gradually to the limiting value of 4.

At corresponding concentrations of salt and ammonia, increase of temperature is accompanied by a decrease of the distribution-coefficient, as was also found to be the case for pure water. The variation is, moreover, of the same relative order of magnitude in the two cases, in consequence of which the question as to the influence of temperature on the dissociation of the molecular complexes in solution cannot be deduced with certainty from the experiments. We hope, however, as the result of further investigations, to be able to ascertain this influence of temperature.

YORKSHIRE COLLEGE,  
LEEDS.

CXX.—*Action of Alkalis on the Nitro-compounds of the Paraffin Series. Part II. Reactions and Constitution of Methazonic Acid and the Mode of Formation of Isoxazoles.*

By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING, B.Sc.

IN 1891 (Trans., 1891, 59, 410), one of us, in conjunction with Mr. T. S. Dymond, gave an account of the action of alkalis on the nitro-compounds of the paraffin series. We showed that, in the case of nitroethane and primary nitropropane, trimethyl- and triethyl-isoxazole respectively are formed. With nitromethane and secondary nitropropane no isoxazole is formed, and the reaction appears to follow a different course. The mechanism of the change by which the isoxazole is formed from the nitro-compound was at the time not clear, and the discussion was therefore postponed.

In the present paper an account is given of the mode of action of alkalis on nitromethane and on secondary nitropropane, whilst what we believe to be a satisfactory suggestion as to the probable course of the remarkable action of alkalis on the nitroparaffins generally is put forward.

*Action of Alkalis on Nitromethane.*

In the paper referred to above, it is pointed out that no isoxazole can be isolated from the product of the action of aqueous alkalis on nitromethane. A very vigorous change occurs, the mixture becoming warm, dark coloured, and finally almost black. A nitrite is

produced, together with much cyanide and a considerable quantity of resin, and also a compound having acid properties, of which we are now able to give a full description.

*Action of Ammonia on Nitromethane.*—The action of ammonia is the least vigorous and best adapted for the study of the products of the change. When nitromethane stands in contact with strong aqueous ammonia for several hours, the liquid becomes dark brown and deposits a crystalline substance. The small crystals thus obtained are coloured, and very difficult to purify. The following plan has been found to answer best.

Twenty c.c. of nitromethane contained in a small bottle are mixed with 8 c.c. of strong aqueous ammonia, and ammonia gas is then passed into the mixture until it is completely saturated. The bottle is now stoppered and kept at a temperature not exceeding  $10^{\circ}$  for about a day, the crystals which have separated are removed and reduced in the moist state to a fine powder. This powder is drained on a porous tile and dried by exposure to air. The residual liquid is again saturated with ammonia gas and allowed to stand, the crystals being then removed, powdered, and dried as before. This process is repeated until the whole of the nitromethane has disappeared. By this means 20 c.c. of nitromethane furnish about 12 grams of the crystalline substance.

By washing with aqueous ammonia the crystals may be obtained quite colourless, but this method of purification is very wasteful owing to the loss by solubility. The crystals are soluble in methyl alcohol, less soluble in ethyl alcohol and nearly insoluble in ether or chloroform. When heated, they decompose with production of hydrogen cyanide. When ferric chloride is added to an aqueous solution it produces a purplish-brown colour which is discharged by heating or by dilute acids. Ammonia is liberated by the action of cold aqueous potash. The crystals are therefore evidently the ammonium salt of an acid.

0.1442 gave 44 c.c. nitrogen at  $24^{\circ}$  and 764 mm.  $N = 34.3$ .

$C_2H_3O_3N_2 \cdot NH_4$  requires  $N = 34.7$  per cent.

Silver nitrate produces an abundant pale yellow precipitate in an aqueous solution. The silver salt thus obtained is purified by washing with water and alcohol, after which it is dried by exposure to the air. If heated near  $100^{\circ}$ , it explodes. It is readily dissolved by dilute nitric acid or by ammonia. On analysis it furnished the following results:

0.2630 gave 0.1080  $CO_2$  and 0.0424  $H_2O$ .  $C = 11.2$ ;  $H = 1.8$ .

0.3722 „ 0.1575  $CO_2$  „ 0.0576  $H_2O$ .  $C = 11.5$ ;  $H = 1.7$ .

0.1280 „ 15 c.c. moist nitrogen at  $19^{\circ}$  and 760 mm.  $N = 13.2$ .

0.2266 „ 26 c.c. „ „ at  $19^{\circ}$  „ 766 mm.  $N = 13.2$ .

0.2041 „ 0.1373  $AgCl$ .  $Ag = 50.6$ .

$C_2H_3O_3N_2Ag$  requires  $C = 11.3$ ;  $H = 1.4$ ;  $N = 13.2$ ;  $Ag = 51.1$  per cent.

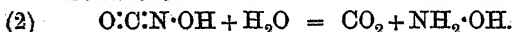
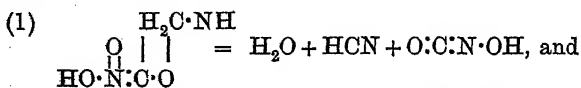
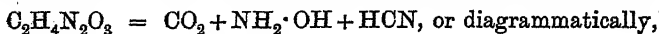
Mercuric chloride produces in a solution of sodium methazonate a yellow precipitate which is chiefly composed of *basic mercuric methazonate*. This salt explodes when heated, and is converted by dilute hydrochloric acid into a soluble, crystalline *mercuric methazonate*. The lead salt is insoluble, and explodes on heating.

*Methazonic Acid.*

The acid is readily isolated from the ammonium salt by mixing a strong aqueous solution with the equivalent quantity of dilute sulphuric acid and extracting with ether. The ethereal solution is dried with calcium chloride and evaporated in a vacuum. By this means an acid crystallising in plates is isolated, which very readily changes into a red resin. It is best purified by recrystallisation from warm benzene or chloroform. The acid may be obtained from the silver salt by the same means. It is identical with the *methazonic acid* briefly described by Lecco (*Ber.*, 1876, 9, 705) as resulting from the action of alcoholic soda on nitromethane; little or nothing, however, was recorded as to its reactions or constitution.

Methazonic acid crystallises in colourless plates which are easily soluble in water, alcohol, ether, acetone, warm benzene, or chloroform. It is strongly acid to litmus and to methyl-orange, and effervesces in contact with alkali carbonates. When quite pure, the acid is colourless, but on standing it soon becomes dark red, and in a short time almost completely changes into a red resin. It melts between 60° and 70°, the precise melting point depending on the rate of heating. During the heating the substance suffers decomposition, becoming at first red; as the heating is continued, the colour darkens, and at about 100° gas is evolved and water is deposited on the cool parts of the tube. At about 110°, the substance suddenly decomposes explosively, evolving hydrogen cyanide and some nitrous fumes, a black residue remaining.

*Action of Acids and Alkalis.*—Numerous experiments have been conducted on the action of acids and alkalis on the acid and its salts. The results justify the conclusion that the substance is decomposed, by hydrolysis following internal oxidation, into carbon dioxide, hydroxylamine, and hydrocyanic acid, as shown by the following equation:



The silver salt was boiled with hydrochloric acid (20 per cent.) for three hours in a flask with an upright condenser attached to a bottle containing soda solution; in this solution, both carbonate and cyanide were found, whilst the residual acid liquid in the flask when



evaporated furnished hydroxylamine hydrochloride together with some red resin. The same products, together with a little formic acid, are obtained by heating the ammonium salt with sulphuric acid (50 per cent.).

0.2272 gram of pure methazonic acid was mixed with concentrated hydrochloric acid and boiled for about an hour. The hydroxylamine in the residue was estimated by decinormal iodine solution in the presence of magnesia. It was proved that 0.0693 gram of hydroxylamine had been produced, which is about 90 per cent. of that required by the equation given above.

When heated with aqueous alkalis, methazonic acid is decomposed furnishing hydroxylamine, carbonate, and cyanide. If the heating is continued, nitrate and ammonia are also produced from the decomposition of the hydroxylamine.

0.1549 gram of the pure acid dissolved in water (free from carbon dioxide) was mixed with baryta water and the mixture heated in a sealed tube for four hours at 100°; the precipitate of barium carbonate was washed from the tube, converted into sulphate and weighed.

0.332 gram of barium sulphate was obtained, equivalent to 0.0627 gram of carbon dioxide, which is 95.7 per cent. of that required by the equation given above. It is therefore clear that alkalis and acids produce similar changes in the compound.

*Oxidation and Reduction.*—On oxidation with permanganate in either acid or alkaline solution, the same products were invariably obtained, namely carbon dioxide, hydrogen cyanide, and nitric acid. The same result ensues when chromic acid or hydrogen peroxide is used as the oxidising agent. Many experiments have been made on the slow reduction of methazonic acid in the hope of obtaining a definite nearly related reduction product. Sodium amalgam, sodium in moist ethereal solution, zinc-dust and water, zinc and tin with dilute hydrochloric acid, as well as other reducing agents have been tried. In every case the same products were obtained, namely, ammonia and formic acid together with more or less resin. No trace of either ethylenediamine or methylamine could be found. It therefore seems probable that hydrolysis preceded, or accompanied, reduction in all these cases.

*Red Resin.*—The red resin which is so readily formed from methazonic acid is apparently very closely related to it in constitution, since it furnishes the same products on hydrolysis, reduction, and oxidation. It is probably a condensation product formed by the elimination of water or possibly a polymeride.

*Action of Alkyl Iodides on Silver Methazonate.*—When ethyl or methyl iodide is added to silver methazonate suspended in ether, reaction slowly occurs with separation of silver iodide. On filtering

and evaporating the solution in a vacuum desiccator a reddish-brown resin is obtained in which long, needle-shaped crystals are imbedded. The crystals may be extracted by warm benzene and obtained from this solution almost colourless. The yield, however, is extremely small, and it appears that the alkyl salts,  $C_2H_5(CH_3)O_3N_2$ ,  $C_2H_5(C_2H_5)O_3N_2$ , of methazonic acid are even more unstable than the acid itself, readily changing into resinous products.

*Constitution of Methazonic Acid.*—Lecco has suggested that methazonic acid is an anhydride,  $\begin{matrix} CH_2 \cdot NO \\ | \\ CH_2 \cdot NO \end{matrix} > O$ , formed from two molecules of nitromethane. This formula is, however, clearly inadmissible.

The reactions of methazonic acid described above lead to the conclusion that the constitution of methazonic acid is represented by the following

formula,  $HO \cdot N \cdot \begin{matrix} \cdot NH \\ | \\ C \cdot O \end{matrix}$ , which satisfactorily explains the formation of the products obtained by hydrolysis, reduction, and oxidation.

#### *Action of Alkalis on Secondary Nitropropane.*

Secondary nitropropane is much less readily attacked by alkalis than the primary nitro-compound. On heating with excess of aqueous soda in a closed tube for two hours at  $115^\circ$ , the liquid still contained some unaltered nitropropane. The products of the action are *acetone*, *nitrous acid*, and *hydroxylamine*, together with a small quantity of *hydrogen cyanide*. If the liquid is acidified, *propyl pseudonitrole* is obtained, owing, no doubt, to the action of nitrous acid on the unchanged nitro-compound. As stated in the paper already referred to, no isoxazole is formed by the action of alkalis on secondary nitro-compounds.

#### *Mechanism of the Action of Alkalis on Nitroparaffins.*

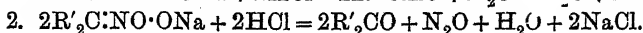
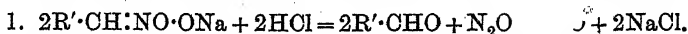
In the previous paper (*loc. cit.*) it was pointed out that the remarkable action of alkalis on nitroparaffins "cannot be satisfactorily explained if the usual formula for nitroethane be rigidly adhered to," but that an explanation could be found if the tautomeric formula, containing a hydroxyl group, were employed.

Since this was written, Nef (*Annalen*, 1894, 280, 263) has published an important paper on the constitution of the salts of nitroparaffins, in which he supposes that their reactions can only be explained by adopting the view that the metal takes the place of the hydrogen of the hydroxyl group attached to nitrogen in the tautomeric formula of the nitro-compound. Thus for sodium nitroethane the formula  $CH_3 \cdot CH \cdot NO \cdot ONa$  is suggested, and for the sodium salt of secondary nitropropane the formula  $(CH_3)_2C \cdot NO \cdot ONa$ .

The experimental evidence which Nef has brought forward in support of the tautomeric formula for the salts of nitroparaffins appears to us to be very strong, and his view seems to be much more in accordance with the facts than the assumption of V. Meyer that the metal is joined to the carbon owing to the influence exercised by the negative nitro-group on the hydrogen which is united to the same carbon atom.

The evidence for Nef's formula may be summarised as follows :

(i) When the cold aqueous solution of the salt of a nitroparaffin is decomposed with cold dilute acids the nit. is regenerated to a very small extent, the greater part of it being decomposed into nitrous oxide and an aldehyde (from primary comp. a ketone (from the secondary compounds) in accordance with the following equations :



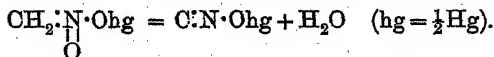
This mode of decomposition indicates that the salts have not the same constitution as the original nitro-compounds, for if this were the case, on the addition of acid they would be completely reconverted into them.

Nef found that the sodium salt of nitroethane is almost quantitatively decomposed by dilute sulphuric acid in accordance with the above equation. This renders it probable that the first product of the action of the dilute acid on sodium nitroethane is the tautomeride,  $CH_3\cdot CH:NO\cdot OH$ , which then undergoes intramolecular oxidation thus  $2CH_3\cdot CH:NO\cdot OH = 2CH_3\cdot CHO + \frac{N\cdot OH}{N\cdot OH} (= N_2O + H_2O)$ .

The sodium salts of nitromethane and secondary nitropropane behave in a precisely similar manner. Moreover, when the mercuric chloride derivative of nitroethane,  $C_2H_4(HgCl)NO_2$ , is mixed with hydrochloric acid, nitrous oxide and acetaldehyde are produced, but no nitroethane.

(ii) If aqueous mercuric chloride is added to an aqueous solution of sodium nitromethane, mercuric fulminate is formed.

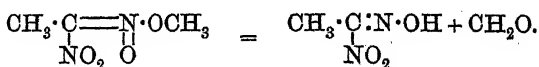
Nef has suggested that mercuric nitromethane is first produced and by intramolecular oxidation loses water, passing into mercuricfulminate.



Nef has adduced additional facts in support of this constitution of the fulminate, in particular the production of monochloroformoxime by the action of dilute hydrochloric acid, whilst more recently Scholl (*Ber.*, 1899, 32, 3492) has confirmed this formula by showing that benzaldehyde is produced by the action of mercuric fulminate on benzene in the presence of aluminium chloride.

(iii) By the action of methyl iodide on the silver salt of dinitroethane,

formaldehyde and ethylnitrolic acid are produced. This is most simply explained by supposing that the methyl ether of dinitroethane is first formed and then undergoes intramolecular oxidation.

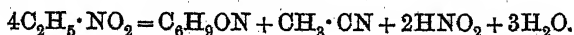


By the same supposition, the action of ethyl iodide on silver dinitroethane forming acetaldehyde and ethylnitrolic acid may be explained.

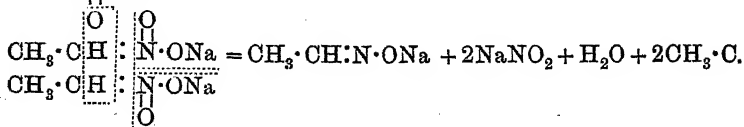
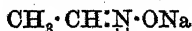
Although Victor *Ber.*, 1895, 28, 202) still maintained the correctness of *his* formula for the metallic derivatives of the nitroparaffins, it must be admitted that all the experimental evidence produced by *him* strongly supports the alternative contention that these compounds should be regarded as derivatives of the tautomerides of the nitroparaffins.

We are therefore justified in assuming the correctness of this tautomeric formula in discussing the mechanism of the remarkable reactions of alkalis and nitroparaffins first described by one of us in 1891.

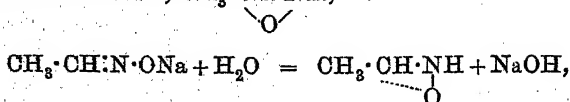
It has been shown that when nitroethane is warmed with aqueous alkali, trimethylisoxazole, acetonitrile, and nitrous acid are formed in the proportions given by the equation



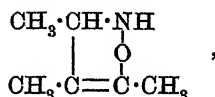
Representing the sodium salt of nitroethane by the formula  $\text{CH}_3 \cdot \text{CH} : \underset{\text{O}}{\underset{\text{O}}{\text{N}}} \cdot \text{ONa}$ , the existence of oxygen doubly linked to nitrogen enables the compound to act as a powerful oxidising agent.



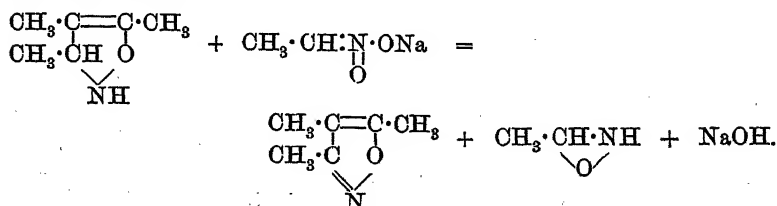
The sodium derivative of acetaldoxime is thus formed, together with sodium nitrite and a residue  $(\text{CH}_3 \cdot \text{C})_2$ . Sodium acetaldoxime dissociates in the presence of water and the oxime tends to change into its tautomeric form,  $\text{CH}_3 \cdot \text{CH} \cdot \text{NH}$ ,



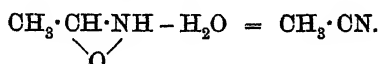
which then joins itself on to the  $\text{CH}_3 \cdot \text{C}$  residues, forming trimethyl-



which, in the presence of unaltered sodium nitroethane, is immediately oxidised, forming trimethylisoxazole and acetaldoxime.



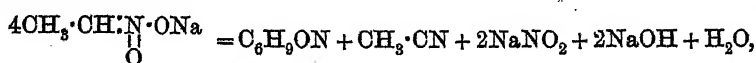
The dehydration of this acetaldoxime accounts for the production of the acetonitrile,



Thus, starting with the tautomeric formula of nitroethane, we can at any rate now understand how the remarkable reaction described in the former paper may take place. The phases of the action may be summarised thus :

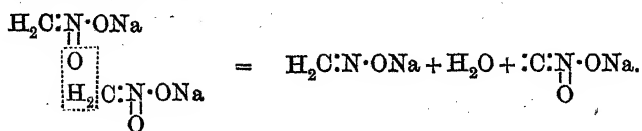
1.  $3\text{CH}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{ONa} = \text{C}_6\text{H}_{11}\text{ON} + 2\text{NaNO}_2 + \text{NaOH}.$
2.  $\text{CH}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{ONa} + \text{C}_6\text{H}_{11}\text{ON} = \text{CH}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{OH} + \text{C}_6\text{H}_9\text{ON} + \text{NaOH}.$
3.  $\text{CH}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{OH} = \text{CH}_3 \cdot \text{CN} + \text{H}_2\text{O},$

or in one equation,

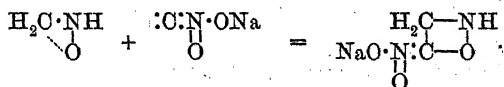


which agrees precisely with that given in the previous paper as the result of experiment.

With nitromethane the result is very different, the action of alkalis producing no isoxazole, but instead methazonic acid. The formation of this compound can, however, be understood if the tautomeric formula is adopted. The sodium salt of nitromethane being  $\text{H}_2\text{C} \cdot \text{NO} \cdot \text{ONa}$ , in aqueous solution it would react by intermolecular oxidation according to the following scheme :

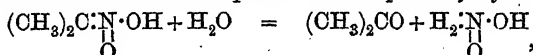


The sodium salt of formaldoxime thus generated will be dissociated into the tautomeric form of the oxime,  $\text{H}_2\text{C}=\text{N}\cdot\text{OH}$ , which, condensing with the nitromethane residue, will form the sodium salt of methazonic acid,

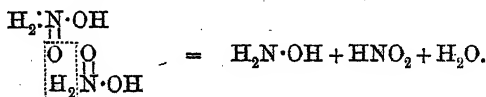


The different behaviour of the sodium salt of secondary nitropropane furnishing acetone, nitrite, and hydroxylamine when acted on by alkalis may be explained by its greater stability owing to the absence of the CH or CH<sub>2</sub> group which makes it less susceptible of intermolecular oxidation.

It is probable that the decomposition takes place by hydrolysis,



the "oxy-hydroxylamine" undergoing immediate decomposition with the production of hydroxylamine and nitrous acid,



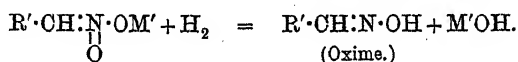
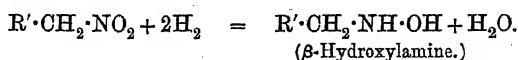
#### *The Reduction of Nitroparaffins and their Salts.*

In the foregoing discussion, the reduction of the metallic derivatives of nitro-compounds to those of oximes is assumed to be possible. It has been previously stated (Dunstan and Dymond, *Proc.*, 1894, 10, 139) that by the reduction of the nitroparaffins under certain conditions, the corresponding aldoximes and ketoximes are apparently produced, and it was suggested that these may possibly be intermediate products between the nitro-compounds and the substituted hydroxylamines, the formation of which has been observed by V. Meyer, Bamberger, and others.

In order to further elucidate this question, we have carried out a number of experiments on the reduction of the oximes, but in no case has the formation of any substituted hydroxylamine been observed. It therefore appears probable, that the substituted hydroxylamines obtained by the reduction of nitro-compounds are not derived from previously formed oximes, and, moreover, our results seem to indicate that the oximes and hydroxylamines are not produced together, but each separately and under different conditions. The nitro-compounds themselves (reduction in acid or neutral solution) yield the hydroxylamines, whilst their salts (reduction in alkaline solution) furnish the

oximes (or their reduction products). This may be readily demonstrated by warming a few drops of nitroethane with either zinc dust and dilute acid or with zinc dust and water. After a minute or two the solution when filtered is found to reduce Fehling's solution powerfully in the cold, owing to the action of  $\beta$ -ethylhydroxylamine. On the other hand, if nitroethane is dissolved in solution of caustic soda and reduced with zinc dust, the filtered liquid has no reducing property.

These results are in accordance with the view that the salts of the nitroparaffins possess a different configuration from that of the nitro-compounds themselves. The first stage of the reduction of the nitroparaffins and of their salts may therefore be expressed by the following equations:



Since the suggestion above mentioned was published, two cases have been recorded in which nitro-compounds have been directly reduced to the corresponding oximes. Hantzsch and Schultze (*Ber.*, 1896, 29, 2252) have shown that phenylnitromethane, when reduced in alkaline solution with zinc dust or sodium amalgam, yields *syn*-benzaloxime. Bamberger and Weiler (*J. pr. Chem.*, 1898, ii, 58, 333) obtained 2-amino-3:5-dimethylbenzaloxime by reducing 2-nitro-3:5-dimethylphenylnitromethane (*o*-2-dinitromesitylene) by means of sodium amalgam. It is noteworthy that in each case the reduction is effected in an alkaline solution.

SCIENTIFIC DEPARTMENT,  
IMPERIAL INSTITUTE, S.W.

## CXXI.—Amount of Chlorine in Rain-Water collected at Cirencester.

By EDWARD KINCH, Royal Agricultural College, Cirencester.

THE determination of chlorine in rain-water collected in the rain-gauge of the Meteorological Station at the Royal Agricultural College was commenced in 1870 and has been continued to the present time. Results of the determinations in the mixed rain-waters of each six months—October to March and April to September inclusive—up to September 30th, 1886, have been published (*Trans.*, 1887, 51, 92). Results from October 1st, 1886, up to September 30th, 1900, are given below, together with some averages:

Period, six months ending	Rainfall in inches.	Chlorine parts per million.	Equivalent to NaCl, grains per gallon.	Equivalent to NaCl, lbs. per acre.
1887. March 31st .....	15.62	9.59	1.106	55.83
September 30th.....	9.51	2.69	0.310	9.53
1888. March 31st .....	13.06	3.59	0.414	17.43
September 30th.....	14.78	2.90	0.335	15.97
1889. March 31st .....	15.13	3.40	0.392	19.17
September 30th.....	15.52	2.08	0.240	12.03
1890. March 31st .....	10.16	2.60	0.300	9.85
September 30th.....	12.87	1.53	0.176	7.34
1891. March 31st .....	9.39	1.82	0.210	6.33
September 30th.....	17.79	1.15	0.132	7.60
1892. March 31st .....	17.38	3.50	0.404	22.69
September 30th.....	13.73	2.10	0.242	10.74
1893. March 31st .....	11.80	2.89	0.333	12.70
September 30th.....	8.35	3.47	0.401	10.80
1894. March 31st .....	14.29	3.67	0.424	19.55
September 30th.....	15.17	1.70	0.196	9.61
1895. March 31st .....	13.06	2.29	0.265	15.45
September 30th.....	10.85	1.94	0.225	7.84
1896. March 31st .....	13.61	3.30	0.380	16.73
September 30th.....	12.43	3.26	0.376	15.12
1897. March 31st .....	16.74	2.93	0.337	18.11
September 30th.....	16.35	2.10	0.243	12.77
1898. March 31st .....	9.43	3.36	0.388	11.75
September 30th.....	10.50	2.08	0.239	8.08
1899. March 31st .....	16.72	3.64	0.419	22.57
September 30th.....	11.52	2.27	0.263	9.72
1900. March 31st .....	13.32	3.34	0.385	22.62
September 30th.....	9.47	2.41	0.278	8.52
Mean of 14 winter periods to March, 1900.....	14.26	3.55	0.412	19.35
Mean of 14 summer periods to September, 1900.....	12.78	2.27	0.261	10.40
Yearly average of 14 years to September, 1900.....	27.04	2.91	0.337	29.75
Mean of 26 winter periods to March, 1900.....	15.83	3.76	0.435	21.29
Mean of 26 summer periods to September, 1900.....	14.78	2.58	0.302	14.31
Yearly average of 26 years, October 1st, 1874, to September 30th, 1900 ...	30.61	3.17	0.369	36.10

The results in the first years were more irregular than later on, partly because the method of determination of chlorine is improved, so in the final averages only the last 26 years have been taken.

It will be seen that the total deposit of chlorides is distinctly greater in the winter months than in the summer months, this being largely dependent on the prevalence of S.W. gales from the Bristol Channel. For example, the rainfall for the week ending December 31st 1893, during which S.W. gales prevailed, was 1.27 inches, and



contained chlorine 8·5 per million. Rain falling during a storm from S.W. by W. on January 16th, 1899, contained chlorine 44·79 parts per million, equivalent to 5·166 grains of salt per gallon. Other examples were given in the previous report.

Taking all the chlorides as being in the form of sodium chloride, the yearly average deposit of common salt per acre for the past 26 years has been 36 lbs., and for the past 14 years it has been nearly 30 lbs.

G. Bellucci (*Staz. Sper. agrar. Ital.*, 1888, 21, 255) made monthly determinations of the chlorides in the rain-water falling at Perugia, about 75 miles from the sea and 412 metres above sea-level, for 10 months in 1886, and 12 months in 1887. For 1887, the total deposit was equivalent to 37·8 lbs. of salt per acre. Generally, there was rather more in the winter than in the summer months, although the largest amount in 1887 was collected in May.

N. Passerini (*Bol. Scuola Agr. Scandicci*, 1893, 12) made determinations of the chlorides in the rain-water near Florence, about 47 miles from the sea on one side and 67 miles on the other, during 1890 and 1891. The chlorine per million varied from 0·168 to 24·177 on different occasions. In 1890, the average was 6·7 per million, and in 1891, 3·7 per million.

J. B. Harrison (Reports of the Agricultural Work in the Botanic Gardens, Demerara) has determined the chlorine in the rain-water collected at the Botanic Gardens, Georgetown, Demerara, for some years. The average rainfall for the six years 1890—1895 inclusive was 111 inches, the mean annual amount of chlorine 4·69 parts per million, and the average amount of common salt deposited per acre 186 lbs.

## CXXII.—*Hexachlorides of Benzonitrile, Benzamide, and Benzoic Acid.*

By FRANCIS EDWARD MATTHEWS.

BENZONITRILE combines directly with chlorine to form a hexachloride, but, unlike benzene and monochlorobenzene hexachlorides the product appears to be formed in one modification only. The hexachloride obtained, however, is a very interesting substance, and taking it as a starting point for further work, some very unexpected results have been obtained.

The method of preparing the hexachloride is as follows. A considerable amount of benzonitrile (of late one pound has been taken at once) is placed in a large flask and covered with water. Chlorine is

then passed into the mixture to saturation and the flask is placed in a good light or even exposed to direct sunlight till all free chlorine has disappeared. The mixture loses its yellow colour in a few hours in summer and in from two to three days in winter, but if allowed to stand longer, it again gradually assumes a yellowish tint, apparently with the formation of a larger quantity of uncrystallisable substance.

The amount of hydrogen chloride produced is inconsiderable. The saturation with chlorine is repeated four or five times, and after each saturation the colour of the chlorine takes noticeably longer to disappear.

The mixture is now subjected to steam distillation till no more benzonitrile comes over, a thick, heavy, yellowish oil remains behind which on cooling becomes semi-solid. This is transferred to a beaker, heated to about  $60^{\circ}$ , and treated with about twice its volume of cold glacial acetic acid; the oil at once goes into solution on stirring, but almost immediately the solution begins to deposit small crystals, and after standing for twelve hours a large crop is obtained.

The crystals are collected, well drained by means of the pump, and recrystallised from the smallest possible quantity of boiling glacial acetic acid, when large, transparent, colourless crystals are obtained, which are pure enough for most purposes, although they are still slightly sticky from the presence of a small quantity of some impurity, probably a chlorine substitution-product of benzonitrile, which is very difficult to remove by any other solvent than acetic acid. One or two further recrystallisations from almost any organic solvent will yield the substance in a state of purity.

Chlorine determinations were made with both the crude and pure substance.

Crude substance 0.1700 gave 0.4575 AgCl. Cl = 66.58.

Pure substance 0.1572 „ 0.4282 AgCl. Cl = 67.30.

$C_7H_5NCl_6$  requires Cl = 67.40 per cent.

Benzonitrile hexachloride when crystallised from glacial acetic acid forms what appear to be rhombic prisms. It melts perfectly sharply and without decomposition to a colourless liquid at  $157^{\circ}$ , but on strongly heating it above its melting point, decomposes, evolving torrents of hydrogen chloride and leaving a residue of trichlorobenzonitrile. It dissolves readily in all the ordinary organic solvents, from any of which it may be recrystallised. It is only very slightly volatile with steam.

It shows great stability towards aqueous acids, and is not affected by strong hydrochloric acid at  $200^{\circ}$  or by boiling dilute sulphuric acid. Chromic acid in acetic acid solution is without action on it. Alcoholic caustic soda decomposes it in two stages; on gently warming the solution, the usual action of alkalis on hexachlorides takes place, with

the removal of three molecular proportions of hydrogen chloride, thus:

The chlorine removed from 0.2406 gram of the nitrile by decomposition with sodium hydroxide gave 0.3263 gram AgCl. Found Cl = 33.55 per cent., the calculated amount being 33.70 per cent.

On further boiling with alkali, the cyano-group undergoes hydrolysis, and a mixture of trichlorobenzoic acids is formed.

On heating the nitrile with ordinary strong sulphuric acid to 170—180°, the substance first melts and then dissolves with practically no evolution of hydrogen chloride. On cooling the solution, no crystallisation takes place, but upon pouring into cold water, each drop of the acid solution becomes instantly covered with a solid coating, like the shell of an egg, which gradually thickens until all the substance is precipitated.

The substance produced in this manner proves to be a hexachloride of benzamide,  $C_6H_5Cl_6 \cdot CO \cdot NH_2$ . The same change is brought about by long-continued boiling with 50 per cent. sulphuric acid.

This hydration, in the presence of strong sulphuric acid at a temperature of 170—180°, seemed so remarkable that the experiment was repeated many times, but invariably with the result that the nitrile is almost quantitatively converted into the corresponding amide. A given weight of the nitrile always yields rather more than an equal weight of the amide, and no other products have been detected as the result of the reaction.

The substance (i. crude; ii. recrystallised from 50 per cent. acetic acid) gave the following results on analysis:

- i. 0.1538 gave 0.4019 AgCl. Cl = 64.65.
  - ii. 0.1280 „ 0.3292 AgCl. Cl = 63.62.
  - iii. 0.3010 „ 0.2840  $CO_2$  and 0.0648  $H_2O$ . C = 25.40; H = 2.39
- $C_7H_7ONCl_6$  requires C = 25.15; H = 2.10; Cl = 63.77 per cent.

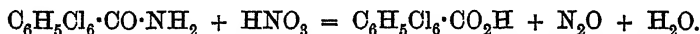
Benzamide hexachloride is a colourless substance slightly soluble in hot water, but almost insoluble in cold. It is readily dissolved by most organic solvents, and crystallises well from aqueous acetic acid (about 70 per cent.) in beautiful, colourless prisms. If these crystals are exposed to the temperature of the water-oven, they break up into a fine, white powder without undergoing decomposition or losing weight appreciably. The substance melts perfectly sharply at 187—188° without decomposition. On boiling with alcoholic soda solution, it first loses three molecular proportions of hydrogen chloride, and finally the amido-group undergoes hydrolysis, and a mixture of the sodium salts of trichlorobenzoic acids is obtained.

Quinoline likewise removes three molecular proportions of hydrogen

chloride from the substance on heating, but here again the product is a mixture, although one modification of trichlorobenzamide is produced in much greater quantity than its isomerides.

The conversion of an amide into the corresponding acid is usually an easy matter, but in the present case considerable difficulty was experienced before the desired result was obtained. Alkaline hydrolysis was precluded owing to the instability of the group  $C_6H_5Cl_6$  towards alkalis, and sulphuric and hydrochloric acids of different strengths and at various temperatures did not give the wished-for product.

The formation of benzoic acid hexachloride was at length found to take place by the action of fuming nitric acid on the amide, and, moreover, the yield appears to be quantitative according to the equation,



The amide, when treated in portions up to 10 grams at a time with 5—6 times its bulk of fuming nitric acid, at once dissolves with evolution of heat, and the solution effervesces; very soon a new substance begins to crystallise out, and the reaction may be completed by gently warming the solution. When all evolution of gas has ceased, the mixture is cooled and poured into cold water; the precipitated acid is then collected, washed free from nitric acid with cold water, and placed on a porous plate to dry (it must not be dried by heating, as it is decomposed by hot water). When thoroughly dry, it can be recrystallised from benzene without undergoing any decomposition.

On analysis, the acid gave the following figures:

0.2443 gave 0.2263  $CO_2$  and 0.0435  $H_2O$ . C = 25.26; H = 1.97.

0.2276 „ 0.5866 AgCl. Cl = 63.76.

$C_7H_5O_2Cl_6$  requires Cl = 63.58; C = 25.07; H = 1.79 per cent.

The examination of the properties of this new acid is not yet complete, but a barium salt has been obtained and analysed. The most striking property appears to be the decomposition it undergoes on boiling with water. Decomposition takes place quantitatively according to the equation, a chlorobenzene tetrachloride being formed,



Work upon this acid and upon the monochlorobenzene tetrachloride is being continued.

THE ROYAL INDIAN ENGINEERING COLLEGE,  
COOPERS HILL, STAINES.

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*L. F. Nilson*

## NILSON MEMORIAL LECTURE.

(DELIVERED ON JULY 5TH, 1900.)

By OTTO PETTERSSON, Professor of Chemistry in the University of Stockholm.

LARS FREDRIK NILSON, born in Ostergothland in 1840, received his education at the high school of Wisby, on the island of Gothland, where his father possessed a large farm, Rosendal. The beautiful scenery and luxuriant vegetation of the sunny island in the Baltic, as well as the historical traditions attaching to its grand mediæval monuments now in ruins, left an impression upon the boy's mind never forgotten in after life. It is, in fact, impossible to understand the character and life-work of Nilson without taking into account his ardent attachment to the island where his youth was spent. As a chemist, he devoted himself with predilection to such investigations as had a bearing upon the development of the great but neglected agricultural resources of Gothland. I shall have more to say of this later; suffice it here to mention that the sugar industry, now so flourishing, and the cultivation of the sugar beet on that island were introduced on his initiative. Still Nilson had no leaning towards commerce; like the true man of science he was, he contented himself with being the adviser and promoter of economic progress. Although his occupations in Stockholm only allowed him time to make a short visit yearly to Gothland, yet he retained until the end of his life the management of a little farm there, which was his inheritance or patrimony, his part of the ancestral soil.

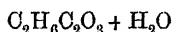
In 1859, at the age of 19, Nilson became a student at Upsala, his studies being directed towards biological science, especially zoology and geology, for which he obtained high marks in the examinations. Although his mineralogical study compelled him to acquire some knowledge of chemistry, he seemed at that time to entertain no special predilection for it. This work, however, brought him into personal contact with the director of the chemical laboratory of the University, Lars Fredrik Svanberg, whose well-known research upon molybdenum was carried out in conjunction with Struve in 1848 in Berzelius' laboratory in Stockholm. Svanberg had been a military engineer until Berzelius, who recognised his great ability as a mineralogist and his extraordinary analytical skill, offered him a place in his laboratory. Their acquaintance soon deepened into a lasting friendship, and greatly did the old master of science need the support of his strong-minded friend in the last critical years of his life, when his system of chemis-

try, once so firmly established, seemed to be on the point of giving way, attacked as it was from all sides by the advocates of the metaleptic and type theories.

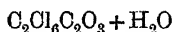
After Berzelius' death, Svanberg was nominated Professor of chemistry in Upsala (1853), and entrusted with the task of erecting a new institution with laboratories for chemistry, mineralogy, and physics. His aim was to raise the study of chemistry at the University, which had flourished under Torbern Bergman, but during the succeeding sixty years had become utterly neglected. This was not easy to accomplish, although Svanberg in many respects possessed excellent qualifications for it; he had an ardent and unselfish devotion to his science, he owned the greatest collection of chemical literature ever possessed by a private person in Sweden, and his phenomenal memory embraced the entire development of chemical science from the first beginning of a rational theory until the time of Berzelius' death. Bearer of the great traditions of the Berzelian era, he, however, had not the power of carrying to victory the ideas which he had defended in company with his illustrious friend.

The question pending at that time was the constitution of the organic bases and acids. Berzelius and Svanberg interpreted both as combinations of an inorganic base or acid with an organic compound, which played the part of 'copula.' Examples of such coupled combinations were to be found also in inorganic chemistry. The first ammoniacal platinum base discovered by Magnus was platinous chloride coupled with ammonia.\* Ethylamine, in the words of Berzelius, was "mit ætheren gepaartes Ammoniak."<sup>†</sup> In close analogy to hydrofluosilicic acid, which was interpreted as hydrofluoric acid coupled with silicon fluoride,  $2\text{HF}, \text{SiF}_4$ ,<sup>‡</sup> acetic acid was regarded as a copula of oxalic acid with ethane, trichloroacetic acid, a copula of oxalic acid with carbon sesquichloride, &c.

It seemed, in fact, to be a desperate position to uphold the apparently extravagant formulæ



and



against the great generalisations of the type theory of Dumas and Williamson expressed in the symbols



Still there was in Berzelius' formulæ, in spite of their errors with regard to atomic weights and to the part played by water in the

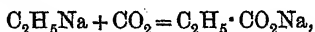
\*  $\text{PtCl}_2\text{NH}_3$ , according to Berzelius.

<sup>†</sup>  $\text{NH}_2\text{C}_2\text{H}_5$ , according to Berzelius.

<sup>‡</sup>  $3\text{HF}, 2\text{SiF}_4$ , according to Berzelius.



constitution of the acid, a germ of truth, and a possibility of progress which the type formulæ lacked. It was Kolbe who was destined to bring out the whole purport of Berzelius' conceptions concerning the copulated organic compounds. In a classical investigation executed partly in Playfair's laboratory in London, and partly in Bunsen's laboratory in Marburg, Kolbe, in 1849, the year after Berzelius' death, proved that acetic acid by electrolysis gave birth to ethane, carbonic acid, and hydrogen \* (*Annalen*, 1849, 69, 252). The further steps of progress from Berzelius' and Kolbe's point of view to that of the modern theory of organic chemistry were the synthesis of sodium propionate by Wanklyn,



and the brilliant discovery of the valency of the elements by Frankland.

From the date of Berzelius' death, Svanberg abandoned experimental work, feeling that his mission was to organise the teaching of chemistry on a broad basis in the new laboratory of the university, and to arouse interest in the study of his science. Like the seer of old, he was content to show to the next generation of his people the path into the land of promise. There can be no doubt that he succeeded, for most of the chemists who now hold the position of teachers at our academies or leaders of the industrial or metallurgical works of our country are pupils of Svanberg. The names which will be most familiar to you are Cleve, Nilson, and De Laval the reformer of the dairy industry of the world.

In 1865, Nilson was ready to take his degree. The examination regulations in Sweden are somewhat complicated, being specially drawn up with a view of insuring that the claims of the humanities shall not be subordinated to those of empirical science; the candidates for the Doctorate of philosophy, therefore, were obliged to undergo examinations in history, philosophy, languages, &c., in addition to their chief subject. The examination itself was a mere formality, but it was preceded by private examinations in every subject, and all these had to be passed within a certain time, usually six months, previous to the day of examination, if not, the whole procedure had to be repeated. Nilson was ready for examination when bad news arrived from home. His father had had a stroke of apoplexy, and the work on the farm was much impeded by his illness. Nilson himself was at that time very delicate in health, suffering from bleeding from

\* It scarcely needs to be mentioned that neither Berzelius nor Kolbe then distinguished between the radical methyl and the compound dimethyl or ethane, the distinction being first made by Frankland several years afterwards.

the lungs. To leave Upsala some weeks before the examination meant to postpone it for a year, or indeed for ever, uncertain as it was if he could hope to return any more. Nilson, however, did not hesitate; he went over to Gothland, and undertook the management of the farm, himself labouring in the fields. When his father, some months afterwards, recovered, to the happy astonishment of the family, Nilson could inform him of two things: firstly, that the harvest was in the barns in the best condition, and the soil prepared and sown for the autumn; secondly, that he had succeeded without any technical assistance in installing the engine and threshing machinery which had just arrived from England—the first machinery of that kind to be introduced into Gothland—and that it had worked excellently. "This"—Nilson wrote to a friend—"awakened the liveliest astonishment in my father." Shortly afterwards Nilson returned to the university, where a richer harvest was ripening for him.

He returned another man than he went. The healthy country life, and labour with its responsibilities and its success had changed the sickly youth, overburdened with mental exertion and doubt about his capacities and calling in life, into a strong, resolute man who knew his aim and how to realise it:

"Der Riese hat die Mutter Erde berührt"

"Und es wachsen ihm neu die Kräfte."

From that time until thirty-two years afterwards, when he literally broke down under the burden of labour, he was never ill, and never tired. Without any difficulty, he passed his examination, obtained his degree with a dissertation on thialdine, and a year later became head of the laboratory as chief assistant and demonstrator of chemistry.

A few words concerning the laboratory of Upsala thirty to forty years ago may not be out of place. There was the large and very crowded common laboratory room irreverently called "the stable" by the students on account of the composition of its atmosphere in which free ammonia entered in a not inconsiderable proportion. Nilson here appeared as a calm and patient teacher rather sparing of words, preferring to give an experimental demonstration or practical advice instead of long verbal explanations. Inside was the assistants' room and Svanberg's private laboratory, where those occupied with scientific investigations had places. Everything here reminded one of Berzelius. There were the balances, the blowpipes, the platinum crucibles—some of the first ever made—that had belonged to him. On the shelves there were some of his preparations, venerable relics from the days of his discovery of selenium, thorium, &c. At a certain hour of the day Svanberg appeared in his old military coat—the abomination of his

august colleagues of the academical *consistorium majus*—eager to know the progress of every new experiment, himself the most enthusiastic of all when success attended the endeavours of his pupils. His rooms on the floor above the laboratory were lined with bookshelves containing thousands of volumes arranged in double rows on each shelf. These treasures of the chemical literature of bygone centuries were destined to belong to the University after his death, and were at the disposal of his assistants and pupils during his lifetime. The circle of scientific students in Svanberg's laboratory was united by ties of friendship in the hours of labour and of pleasure. As work usually continued until late in the evening, there seemed to be little time left for pleasure, but the balance between work and pleasure was kept up in another way. Whilst it was customary in the private laboratory where Nilson presided to enliven the hours of work with conversation, anecdotes, puns, occasionally by a song, &c., it was considered unfitting to introduce scientific matters into the conversation of leisure hours. Nilson positively did not admit it, and woe to him who dared to speak of political or philosophical matters when Nilson intended to be merry. And he was always merry when he was with his friends, the merriest of them all. He had a thousand devices for putting a stop to a conversation which threatened to take a tiresome turn. He would, for example, sit listening for a while with a grave face, and then interpose with a short nonsensical observation, delivered with great solemnity in the accents of some political or scientific worthy of pedantic fame, while a gleam of fun shot forth from under his heavy, dusky eyebrows. The effect was irresistibly comic, so much the more as it came unforeseen. His hearers were at first puzzled, then one chuckled, another laughed, and in a minute the impending political or philosophical discourse was drowned in a chorus of laughter in which Nilson's voice at last joined in accents swelling like big waves and rollers of an ocean of mirth.

Out of the great number of scientific researches undertaken by Nilson, I will speak only of some of the most important, in order to show what scientific impulses he received and how his life-work is connected with the work of the leading masters of his science in present and bygone ages.

In 1871, his first paper in inorganic chemistry "On the Sulphides of Arsenic" was published in the *Proceedings* of the Royal Academy of Sciences in Stockholm. This research was undertaken in order to complete the investigation upon sulphides and sulfo-salts which Berzelius had commenced in 1821—1826.

This period represents the most brilliant epoch in the history of Berzelius, when his generalising genius shone forth in its full vigour,

and made him for a time the undisputed authority on chemical theories. Until that time he had been an adversary of the conception of the binary composition of haloid salts, but in 1821 he at last admitted the cogency of the experimental proofs furnished by Sir Humphry Davy and Gay-Lussac of the elementary nature of the halogens and the binary composition of their hydrogen compounds HCl, HF, &c. His mind was then opened to a wider view of the nature of inorganic compounds which embraced all kinds of salts, and resulted in a new classification of the elementary and compound substances constituting the realm of inorganic chemistry. In Berzelius' Annual Report for 1826, his system of classification is enunciated in short and pregnant definitions: Elements are either positive (metallic) or negative (non-metallic).

Among the non-metallic elements are the two groups:

(1) Halogens\* (*Corpora halogenia*) which form binary saline compounds with the positive metals, and,

(2) Amphids† (*Corpora amphigenia*) which form basic compounds with positive and acid compounds with negative elements.

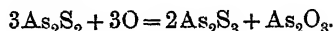
Berzelius says: "There are three classes of salts. The first class, which I denote as *haloid* salts, are combinations of an electro-positive metal and a halogen. The second class, which I denote by the name of *amphid* salts, are constituted of one base and one acid. There are four different amphid salts: oxy-salts, sulpho-salts, selenium salts, and tellurium salts. When we consider the influence this classification has exercised on the theory and the teaching of inorganic chemistry during the greater part of the nineteenth century, we can judge of the enthusiasm which greeted it at the time of its first appearance. Svanberg, however, considered that the analogies which Berzelius had found to exist between the salts of the amphid group needed elucidation and to some extent correction. At his suggestion Nilson undertook the study of the selenium salts and sulpho-salts, of which Berzelius had synthetically prepared 120 without, however, being able to enter upon a closer study of more than a small number of them.

According to Berzelius, there existed three kinds of arsenical sulpho-salts, namely, sulpharsenates, sulpharsenites, and hyposulpharsenites, and four sulphides, namely,  $As_2S_5$ ,  $As_2S_3$ ,  $As_2S_2$ , and  $As_2S$ . Nilson showed that the hyposulpharsenites, as well as the sulphide  $As_2S$ , do not exist. The red or brown precipitate which separates out from boiling solutions of the trisulphide  $As_2S_3$  in sodium carbonate consists of impure realgar,  $As_4S_6$ , and the black sulphide,  $As_2S_3$ , which was supposed to arise from the decomposition of realgar with alkali, is a mixture of this substance with arsenic. He synthesised realgar in a number of different ways,

\* Chlorine, iodine, fluorine (according to Berzelius, 1826).

† Oxygen, sulphur, selenium, and tellurium.

and found that this sulphide is liable to decomposition in air, whereby arsenic trisulphide,  $\text{As}_2\text{S}_3$ , and arsenic trioxide,  $\text{As}_2\text{O}_3$ , are formed,



This change seems to throw some light upon the genesis of orpiment in nature by metamorphosis and decomposition of realgar. In fact, orpiment seems to be a secondary product, since almost every crystal of realgar is found to be coated with a bright yellow deposit of the trisulphide, which increases in bulk with time. Of real sulpho-salts of arsenic derived from the tri- and penta-sulphide, Nilson synthesised a great number. Likewise he discovered the existence of new oxysulphides ( $\text{As}_2\text{S}_2\text{O}_3$ ) and oxysulpho-salts of arsenic.

Nilson's next work, "Researches on the Salts of Selenious Acid," (*Nova Acta Reg. Soc. Ups. III*, 1875), may also be regarded as a complement to the work of Berzelius. In 1817, Berzelius discovered selenium and selenious acid,\* of which he described a number of salts. For the most part he did not go beyond qualitative experiments, and only rarely stated the quantitative composition of a few salts (of sodium, barium, lead, silver) with a view of ascertaining the basicity of the new acid. Nilson considerably enlarged our knowledge of the neutral and acid combinations of selenious acid by accurate analyses of more than one hundred of its salts.

In the beginning of the seventies a new era dawned for inorganic chemistry with the discovery of the periodic relations of the elements by Newlands, Mendeléeff, and Lothar Meyer. The natural system of Mendeléeff in which the new idea for the first time had found its fullest and most perfect expression, completed and supplanted Berzelius' classification of the elements just as the natural system of plants by Jussieu had supplanted the Linnæan system of the vegetable kingdom. Moreover, the periodic law as promulgated by Mendeléeff invited experimental inquiry. There were new elements to discover, atomic weights to correct, elements of doubtful chemical character to study.

The crucial test of the periodic law seemed to lie with the elements of the rare earths. As these elements until then had been found to exist almost exclusively in Scandinavian minerals in which the oxides yttrium, erbium, terbium, cerium, lanthanum, didymium, and thorium had been discovered by Gadolin, Berzelius, and Mosander, it seemed incumbent upon the Swedish chemists to take up the intricate problem once more. Cleve and Höglund undertook a research upon yttrium, thorium, and erbium, which inaugurated the well-known series of investigations still being carried on by Cleve and his pupils.

Shortly afterwards Nilson began the study of the rare earths con-

\* "Selenic" acid in the terminology of Berzelius,

tained in euxenite, of which mineral he had received a considerable quantity from Professor Waage in Christiania. He soon succeeded in extracting a large quantity of the crude oxides, and these were submitted to the fractionating process invented by Berlin, and afterwards practised by Bahr and Bunsen, namely, heating the nitrates until partially decomposed. Nilson began this work with a special purpose in view. He and I had agreed to make a research in common upon the physical and chemical constants of such elements and compounds of the rare earths as were considered to have a special bearing upon the periodic law of Mendeléeff. The material for this investigation was to be partly beryllium oxide, which we prepared in common from crude beryl, and partly such oxides of the rare elements as Nilson hoped to separate in the purest possible condition from the euxenite oxides by systematic fractionation.

The bivalency of beryllium, with the atomic weight 9.2, was a cardinal point of the periodic law. The existing experimental determinations of the atomic heat of metallic beryllium seemed to confirm this view, since the specific heat was found to be 0.642 which, if  $\text{Be} = 9.2$ , makes the atomic heat 5.9 in accordance with the criterion of Dulong.

Nilson and I prepared metallic beryllium from equivalent quantities of beryllium chloride and sodium heated to redness in an hermetically closed crucible of wrought iron. The metal thus obtained had a specific heat 0.41, or only two-thirds of that formerly found, a value which agrees far better with the view that the element is trivalent with an atomic weight of about 13.8, contrary to the requirements of the periodic law.

Still the question of the real atomic weight and valency of this element could be considered open to doubt, since there existed the possibility that beryllium might be an exception to the rule of Dulong, like carbon, boron, and silicon, and that its specific heat would be found to increase with temperature. This explanation received support from a remarkable discovery by Brögger and Flink, who, on examining the crystallised metal prepared by us, found it to possess the same crystalline type (of the hexagonal system) as the bivalent metals, magnesium, zinc, and cadmium. We resolved therefore to determine the specific heat of the metal at higher temperatures than  $100^{\circ}$ , and also the vapour density of its chloride, in order to finally decide the chemical character of the element.

We found that the specific heat increases rapidly with rise of temperature, from 0.42 between  $100^{\circ}$  and  $0^{\circ}$  to 0.50 between  $300^{\circ}$  and  $0^{\circ}$ . Professor Humpidge, of Aberystwyth, who, immediately afterwards, with great experimental skill revised the physical constants of the element, arrived by other methods than ours at concordant results.

The following table contains the numbers thus found representing the atomic weight and specific heat of beryllium :

Atomic weight = 9.081 ( $H=1$ ), Nilson and Pettersson (*Ber.*, 1880, 13, 1451; 1884, 17, 987), = 9.027 ( $H=1$ ), Krüss and Morath (*Annalen*, 1890, 262, 38).

Density  $d_{20^{\circ}/20^{\circ}} = 1.85$ , Humpidge (*Proc. Roy. Soc.*, 1885, 39, 4).

Specific heat :

Temperature.	Nilson and Pettersson. Ice-calorimeter.	Temperature.	Humpidge. Method of mixtures.
0—100°	0.4246	11—100°	0.4236
		11—145	0.4515
		11—193	0.4696
0—300	0.5060	15—240	0.4885
		14—312	0.5105
		11—360	0.5199
		17—447	0.5408

The vapour density of the chloride was found to be (Nilson and Pettersson) :

Temperature.	Density.	Temperature.	Density.
490°	6.700	745°	2.758
520	4.174	812	2.793
589	3.067	1080	2.684
597	3.031	1115	2.779
604	3.090	1184	2.824
686	2.853	1502	2.791
720	2.926		

As the determination of the vapour density of this chloride was the first of a great series of similar experiments, a few words about the methods employed may find a place here.

The determination of vapour densities at high temperatures was at that time (1880—1890) a matter of unusual interest to chemists, since Victor Meyer (1876) had improved the experimental technique by introducing the principle of displacement (*Luftverdrängungsverfahren*), devised by Dulong (compare Dumas, *Compt. rend.*, 1874, 78, 536) into use in a practical and elegant form. Although this method led Meyer and his pupils to some of the most important discoveries of that time, among which the breaking up of the molecules of the halogens at high temperatures was the most remarkable, his method was by no means adapted for accurate measurements. The methods which we employed in the determination of the vapour density of beryllium chloride and subse-

quent experiments with the chlorides of aluminium, indium, germanium, gallium, &c., were described in a paper entitled "Ueber ein neues mit exacter Temperaturbestimmung verbundenes Verfahren zur Feststellung der Dampfdichte flüchtiger Körper" (*J. pr. Chem.*, 1886, [ii], 33, 1). The platinum vessel in which the chloride was allowed to evaporate also acted as the bulb of a gas thermometer of the compensatory type devised by me (*J. pr. Chem.*, 1882, [ii], 25, 102). In our experiments with beryllium chloride and other metals, we found it to be an indispensable condition for obtaining constant results (1), to prepare the chloride from the pure metal by means of dry hydrogen chloride; (2), to employ platinum tubes for the preparation of the chloride and platinum bulbs for the density determination; (3), to evaporate the substance in an atmosphere of an absolutely dry indifferent gas (usually carbon dioxide).

In beryllium chloride, as in most other volatile substances, there seems to exist at low temperatures an unstable association of molecules. For the study of this transitory state, the displacement method of Dulong—V. Meyer is not sufficient, and must be supplemented by that of Dumas. We employed for determinations of the vapour density of chlorides, &c., at such temperatures the modification of Dumas' method introduced by O. Pettersson and G. Ekstrand (*Ber.*, 1880, 13, 1191). From 730° upwards, beryllium chloride was found to have almost exactly the constant density 2.77, as calculated for the molecule  $\text{BeCl}_2$ .

While the beryllium work was proceeding, important discoveries had been made in the chemistry of the rare earths. The mineral samarskite from N. America was found to contain, besides the element terbium already announced by Mosander,\* a whole group of new elements. The first discoveries of these earths were due to Delafontaine in 1878. The confusion about the names, the atomic weights and characteristic absorption bands of the new elements of the samarskite group, which at first appeared in the descriptions given by Delafontaine, Laurence Smith, and others, gradually subsided under the critical scrutiny of Roscoe, Soret, Lecoq de Boisbaudran, and Marignac.

Moreover, the gadolinite group of earths, which was considered until then to contain only two elements, yttrium and erbium, began to break up into a number of new earths. Soret had announced the existence of a new element, X (later identified with the holmium of Cleve) rich in absorption bands, and Cleve found that the bands of the erbium of 1873, of the atomic weight 170.5, began to split up into one group belonging to an element forming a red oxide with the characteristic emission spectrum (by incandescence) of the old erbium, and another group of only two absorption bands in the visible spectrum

\* Mosander's denomination for this element was "erbiun."



belonging to a colourless oxide, to which he later gave the name thulium. The most promising discovery was, however, due to Marignac, who in 1878 found that the entire group of absorption-bands of the erbium earths could be eliminated by successive fractionating, whilst the atomic weight of the remaining oxide increased. He justly concluded that a new element of high atomic weight (172·5) must exist, which he denominated ytterbium. From want of material, he could not purify and isolate its oxide; he therefore exhorted such chemists as possessed a greater supply of material to continue the investigation of the new earth. Now it became Nilson's turn to earn the reward of his long labour; he had started his work with a greater quantity of raw material than other chemists of that time, and he had worked, as was his wont, in the most methodical manner. Moreover, the material, oxides from euxenite, which he treated was singularly rich in the elements of higher atomic weight of the gadolinite group of earths. The consequence was that he could fractionate easily a considerable quantity of nitrates up to the point indicated by Marignac, where the absorption-bands began to vanish, and the atomic weight of the metal amounted to 172·5. Before he had reached that point, however, Nilson made the startling observation that there separated out, among the insoluble basic salts, the nitrate of a less basic metal of lower atomic weight. The equivalent weight of the oxides in the insoluble part of the decomposing nitrates had a tendency to sink instead of to rise. He immediately concluded that, together with ytterbia, a new oxide must exist. The atomic weight of the elements contained in these fractions rapidly sank to 134, and even lower, whilst the atomic weight of the element in the other part of the fractions slowly rose to 173·01, the oxide became snow-white, and all absorption-bands vanished from the solutions of its salts. Nilson thus had succeeded in isolating two of the best defined elements of the rare earths, ytterbium (*Ber.*, 1879, 12, 550) and scandium (*ibid.*, 554). Both are characterised by brilliant emission spectra studied by R. Thalén, and by highly interesting chemical properties. Both elements fill prominent places in the third group of the periodic system, and scandium is especially remarkable, as it is identical with Mendeléeff's hypothetical element ekaboron.

The intention of Nilson and Pettersson to isolate the elements of such oxides as could be obtained in a state of chemical purity from the rare earths and determine their physical and chemical constants was not to be fulfilled. In 1881, I was called to undertake the duties of Professor of chemistry at the newly instituted Stockholms Högskola, Nilson remaining in Upsala as Professor of analytical chemistry. Before parting, we found time to determine the specific volume and heat of the oxides and sulphates of all earth-metals then known (*Ber.*, 1880, 13, 1459).

Occupied as he was with the discovery of ytterbium and scandium, Nilson still found time to publish some important researches upon the chemistry of other members of the rare elements.

Already, in 1877 (*J. pr. Chem.*, [ii], 15, 177), he had taken up the study of the platinichlorides of these elements commenced by Cleve, Jolin, and others.

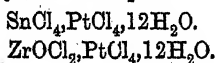
The platinichlorides are of three general types :

- A.  $\left\{ \begin{array}{l} 2\text{RCl}, \text{PtCl}_4 \\ \text{RCl}_2, \text{PtCl}_4 \end{array} \right\}$  (normal platinichlorides).  
 B.  $\text{RCl}_3, \text{PtCl}_4$  ( $\frac{2}{3}$  " " ).  
 C.  $\text{RCl}_4, \text{PtCl}_4$  ( $\frac{1}{2}$  " " ).

To A belong the salts of uni- and bi-valent metals, such as potassium, barium, &c. The platinichloride of beryllium,  $\text{BeCl}_2, \text{PtCl}_4, 8\text{H}_2\text{O}$  (Marignac and others), belongs to this type.

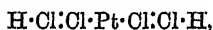
To B belong the platinichlorides of the trivalent elements, aluminium, chromium, iron (Nilson), didymium, erbium, cerium, lanthanum (Cleve, Jolin, and others). Yttrium and indium are exceptions, their platinichlorides being represented by the formulæ  $4\text{YCl}_3, 5\text{PtCl}_4, 52\text{H}_2\text{O}$  (Cleve, Nilson),  $\text{InCl}_3, 5\text{PtCl}_4, 36\text{H}_2\text{O}$  (Nilson).

Of the type C ( $\frac{1}{2}$ -normal platinichlorides), only one member was known, namely, the thorium salt,  $\text{ThCl}_4, \text{PtCl}_4, 12\text{H}_2\text{O}$ , described by Cleve. Nilson found that the quadrivalent metallic elements as a rule form platinichlorides of this type, for example :



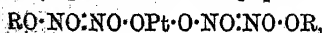
The platinichlorides of metallic elements thus furnish a very characteristic indication of their valency.

The same holds also to a certain extent with regard to the platinochlorides, a class of compounds which, before Nilson's time, had been very little studied. Nilson prepared (*J. pr. Chem.*, 1877, [ii], 15, 260) the corresponding chloroplatinous acid,



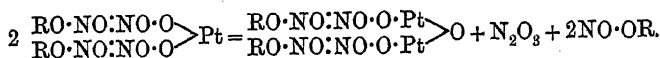
which exists only in dilute solution, and on evaporation in a vacuum decomposes, losing hydrogen chloride forming the compound  $\text{H} \cdot \text{Cl} \cdot \text{Cl} \cdot \text{Pt} \cdot \text{Cl}$ , which at  $100^\circ$  is transformed into platinous chloride,  $\text{PtCl}_2$ .

From the same year (1877), dates an important research upon plato- and diplato-nitrites. The constitution of the platonitrites, first studied by Lang (*J. pr. Chem.*, 1861, 83, 415), had been interpreted by Blomstrand (*J. pr. Chem.*, 1871, [ii], 3, 186) to be

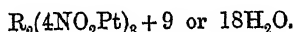


the formulae of platotetranitrosylic acid.

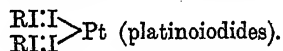
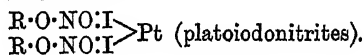
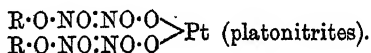
The platonitrites are beautifully crystallised salts. Nilson found that in some cases they decompose into diplatonitrites, nitrous acid, and nitrites (*Ber.*, 1876, 9, 1722).



In this way, the diplatonitrites of silver, beryllium, and iron ( $\text{Fe}'''$ ) are formed. The tervalent metals, yttrium, erbium, lanthanum, and didymium form normal platonitrites of the composition



Nilson found that the platonitrites of potassium and barium are changed into iodoplantonitrites (*Ber.*, 1878, 11, 879) if treated with iodine in alcoholic solution. This new class of salts occupies an intermediate position between the platonitrites and platinoiodides.



In 1882, Nilson published his first researches upon thorium which he later completed in conjunction with G. Krüss (*Zeit. physikal. Chem.*, 1887, 1, 301). He succeeded in obtaining metallic thorium and determining the vapour density of its chloride.

In preparing pure thoria, Nilson experienced the difficulty of removing from it the last traces of cerium dioxide, which most pertinaciously clings to it. The fact that this was successfully overcome in 1883 has been of some importance in the industrial rivalry of the great incandescent lighting companies, since the first patent claimed the employment of pure thoria, which is, however, by no means a fit material for incandescent lamps.

Nilson and Krüss (*Zeit. physikal. Chem.*, 1887, 1, 391) also tried to isolate niobium from potassium fluoroniobate, but, like Marignac, they obtained the hydride,  $\text{NbH}$ , instead of the metal. The specific heat of this hydride was found to diminish considerably with rise of temperature, as shown by the following numbers:

Temperature .....	0—100°	0—210°	0—301°	0—440°
Spec. heat of $\text{NbH}$ .....	0.0977	0.0925	0.0871	0.0834
Molecular heat of $\text{NbH}$ ...	9.3	8.8	8.3	7.9

In the course of his long work upon the elements of the rare earths, Nilson had acquired a rich collection of their oxides, extracted from

different minerals. When Nilson and Krüss (*Ber.*, 1887, 20, 3067) spectrometrically compared the relative intensity of the characteristic absorption-bands of holmium, thulium, didymium, erbium, samarium, &c., in the solutions of basic nitrates of oxides derived from different minerals, they discovered remarkable variations, similar in character to those observed in 1886 by Crookes (*Proc. Roy. Soc.*, 1886, 40, 563) who stated that it was possible to eliminate band after band from the original didymium spectrum until only a single band  $\lambda$  443 was left. From similar observations, Nilson and Krüss drew the following conclusion: "Nach obigen Auseinandersetzungen hätten wir an Stelle des Erbiums, Holmiums, Thuliums, Didyms, und Samariums, die Existenz von mehr denn zwanzig Elementen anzunehmen."

Few chemists of the present day will admit the strictness of this conclusion. There are many facts indicating that absorption bands as well as luminous bands of fluorescence cannot be regarded as essential characteristics of elementary substances. The experiences of Sorby with jargonium, as well as the observations of Liveing upon the variations occasioned by the nature of the solvent, and by impurities, on the intensity of absorption bands, are instructive in this respect. We can also hope that the study of the radio-active substances which are found to accompany the rare elements may throw light upon this question, so that the nebula of elementary matter which now seems to exist within the erbium and other groups will dissolve into well-defined elements.

Once more, after Nilson had taken up his residence at Stockholm as Professor of agricultural chemistry, an opportunity arose for carrying on the investigation upon the physical and chemical properties of the rare elements which we had planned in earlier days. The time for our joint work was, however, very limited owing to official duties, and the fact that new scientific interests had arisen on both sides. Nilson's efforts were concentrated upon the problems of augmenting the harvests and the fertility of the soil, whilst mine were concerned with the physical and chemical properties of the ice and water of the ocean. Still, we were able to spare about three weeks every year for research, and of these we made five by working late.

Much uncertainty prevailed with regard to the formulæ and molecular weights of the chlorides and similar compounds of aluminium, indium, gallium, iron ( $\text{Fe}'''$ ), and chromium. The vapour densities of aluminium chloride and ferric chloride had been found by Deville and Troost (*Ann. Chim. phys.*, 1860, [iii], 58, 283) as well as by V. Meyer (*Ber.*, 1879, 12, 1199) to correspond with those required for the formulæ  $\text{Al}_2\text{Cl}_6$  and  $\text{Fe}_2\text{Cl}_6$ , whilst indium chloride, according to V. Meyer, must be represented by the formula  $\text{InCl}_3$ . About gallium chloride opinions were divided, Lecoq de Boisbaudran's determination (*Compt. rend.*, 1881, 93, 329) being in accordance with the

doubled formula  $\text{Ga}_2\text{Cl}_6$ , Friedel's (*ibid.*) more with  $\text{GaCl}_3$ . The question seemed the more ambiguous as the determinations according to Dumas' method always seemed to give greater values for the density than those obtained on Dulong's principle at the same temperatures.

We found that no range of temperatures exists through which the vapour density of these chlorides is sufficiently constant to warrant the doubled formulæ  $\text{Al}_2\text{Cl}_6$ ,  $\text{In}_2\text{Cl}_6$ , &c. Whilst the density of aluminium chloride as observed by Deville and Troost is 9.20 between  $350\text{--}440^\circ$  (corresponding with that required for the formula  $\text{Al}_2\text{Cl}_6$ ), it increases below that temperature, and decreases above it (*Zeit. physikal. Chem.*, 1889, 4, 206) until at about  $800^\circ$  (or even below that temperature, if evaporated in an indifferent gas) the value 4.60\* is obtained which remains constant for some hundred degrees.

The vapour of aluminium chloride at low temperatures—like that of acetic acid studied by Cahours—consists of unstable associations of molecules,  $n\text{AlCl}_3$ , which generally undergo dissociation into  $\text{AlCl}_3$  as the temperature increases. This dissociation depends, not only upon temperature, but also upon pressure, consequently dissociation will be found to be more advanced at a certain temperature if the chloride is evaporated in an atmosphere of an indifferent gas, as is the case in experiments with the displacement method. This accounts for the discrepancy between the vapour densities determined on Dumas' and on Dulong's principles (*Zeit. physikal. Chem.*, 1889, 4, 224).

At very high temperatures we observed a gradual breaking up of the molecules of these chlorides, characterised by a slight diminution of the vapour density. The temperature at which this chemical dissociation begins is very different in different chlorides, for while beryllium chloride maintains its normal vapour density 2.77 up to  $1500\text{--}1600^\circ$ , aluminium chloride begins to show signs of chemical dissociation above  $1000^\circ$ , and gallium chloride below this.

We found that indium has three chlorides:  $\text{InCl}_3$ ,  $\text{InCl}_2$ ,  $\text{InCl}$  (*Trans.*, 1888, 53, 814; *Zeit. physikal. Chem.*, 1888, 2, 65), and gallium two chlorides:  $\text{GaCl}_3$  and  $\text{GaCl}_2$ , each characterised by the normal vapour density required for the respective formulæ. Thus it is proved that a metal such as indium can exist in gaseous compounds as a uni-, bi-, and ter-valent element.

In 1886, Clemens Winkler discovered germanium, the ekasilicon of Mendeléeff, and entrusted to us the determination of its physical constants, namely, the specific heat of the metallic element and the vapour density of its chloride,  $\text{GeCl}_4$ , and sulphide,  $\text{GeS}$ . The results of this investigation are published in 1887 in a paper entitled: "Ueber

\* The theoretical value for  $\text{AlCl}_3$  is 4.60.

einige physikalische Constanten des Germaniums and Titans" (*Zeit. physikal. Chem.*, 1887, 1, 27).

From 1878 to 1883, Nilson filled the position of Professor of analytical chemistry at the University of Upsala. In 1883, he became Professor of agricultural chemistry at the Royal Academy of Agriculture in Stockholm. He devoted himself to his new duties with the same energy and interest which he had shown in his investigations in theoretical chemistry. In the first place, he had to organise the laboratory and make arrangements for experiments with plant culture in accordance with modern methods, and then he elaborated minute directions for the analytical work in the different chemical stations of Sweden, of which he was inspector. He was consulted in all questions of importance concerning agricultural or technical legislation, and his decision on such questions was always founded upon exact and original experimental investigation, as will be found from his reports upon the analysis of butter and of milk, or his examination of the lactocrite method, and the efficiency of the different mechanical methods of separating the fatty matter from milk, or his investigation in reference to urban sanitation.

It could hardly be expected that, in addition to this official work, he could find time and opportunity for experimental scientific investigations in agricultural chemistry, nevertheless, there are not less than 57 separate papers upon such topics published by him in the *Journal* of the Royal Academy of Agriculture.\* I must confine myself here to mentioning only two or three of these investigations.

In the first place, both on account of the intrinsic value of the analytical work bestowed upon the subject, and on account of its practical importance, his treatise on the possibility of introducing the culture of the sugar beet into Gothland must be mentioned. The climate and the arable land of Gothland are in themselves favourable to the culture of this plant, as pointed out long before by A. Müller and others. More than 30,000 hectares, or about one-ninth of the area of this island, consist of almost sterile swamps, the soil being composed of a thin layer of humus formed by decayed vegetable matter which has grown in the stagnant water in the hollows of the plateau of Silurian limestone forming the geotectonic framework of the island.

Nilson proved by chemical analysis as well as by cultural experiments, that the black soil of these swamps is unusually rich in lime and nitrogenous humous substances, containing as much as 4 or 5 per cent. of nitrogen. The sterility of the soil in its natural state is due to the almost total absence of phosphoric acid, and, in some measure, also to the scarcity of potassium. If this want is supplied by artificial

\* See *Kongl. Landbruksakademiens Handlingar och Tidskrift*, 1883-1898.

nanuring, the richest crops of corn, rape, and sugar-beet can be obtained. The intelligent farmers of Gothland, to their great economic profit, hastened to follow Nilson's advice ; the barren ground of the swamps is now drained and sown with corn and rape, and, to some extent also, with sugar-beet.

An indispensable condition for maintaining a rational culture of the soil is to have a supply of natural or artificial calcium phosphate. The annual import of phosphates into Sweden is equivalent to more than 18 million kilograms of phosphoric oxide, whilst only 2 or 3 million kilograms are produced in the country, the condition of things not being favourable for the manufacture of basic phosphate. In the Northern provinces of Sweden, especially in the great iron-ore district of Gellivara, apatite occurs so intimately mixed with iron ore, that the latter must be separated from it either by washing or by magnetic extraction. It occurred to Professor J. Wiborgh that the apatite powder could be converted into tetraphosphate by ignition with alkali. When the first experiments had proved successful, Nilson, at Wiborgh's request, took over the analytical investigation and biological experiments with the new fertiliser. Thirty parts of soda are heated to about 900—1000° with 100 parts of powdered apatite, which, on the average, contains about 17 per cent. of felspar.\*

The chemical reaction is :

1.  $\text{CaF}_2, 9\text{CaO}, 3\text{P}_2\text{O}_5 + 3\text{Na}_2\text{O}, \text{CO}_2 = 2\text{Na}_2\text{O}, 10\text{CaO}, 3\text{P}_2\text{O}_5 + 2\text{NaF} + 3\text{CO}_2.$
2.  $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2 + 2\text{Na}_2\text{O}, \text{CO}_2 = \text{K}_2\text{O}, 2\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2 + 2\text{CO}_2.$

The product, which consists of neutral silicates and tetraphosphates of calcium, sodium, and potassium, is insoluble in water, but is still assimilable by plants more completely than ordinary tetraphosphate obtained by the Thomas-Gilchrist method. For the manufacture of Wiborgh phosphate a great industrial establishment is now in working at Luleå.

Nilson was a member of the Chemical Societies of England, France, and Germany, and of nearly all learned Societies and Academies of the Scandinavian countries. He was a most active and influential member of the Royal Academies of Science and of Agriculture in Stockholm, but as much as possible avoided representative duties, declining, for example, much to the disappointment of his colleagues, to undertake the Presidency of the former. He was not a brilliant lecturer, but no one was listened to with greater attention.

\* The presence of silicate—as might be foreseen from the recent researches of Wagner and others—is essential for the assimilability of the tetraphosphate by plants.

In the scientific world, it awakened not a little surprise commingled with regret that Nilson, in 1883, a few years after his discovery of ytterbium and scandium, left his work in the field of theoretical chemistry, where he had met with such brilliant success, in order to take up the seemingly modest occupation of an agricultural chemist. His friends knew that this involved a great sacrifice on his part, but they felt no astonishment at his resolution. They knew that with Nilson the sense of duty was paramount, and the desire of success of secondary importance. His country needed him to fill that place—that was all. Besides, there dwelt within him an innate love of living nature; he liked not only to study the abstruse problems of natural science, but he was also an admirer of nature herself. He was fond of farming and gardening; he loved flowers, and had a singular talent for arranging them. In this art he considered his own taste infallible, he could admit the talent of others, but he acknowledged the superiority of none. I can see him on one of those days when he had invited a party of friends to his hospitable house, entering the room with a huge burden of flowers from the meadow or garden, arranging them deliberately in his own original fashion, before he came forth beaming with pleasure to welcome his guests.

The burden of labour which his excellent constitution had long sustained without any sign of giving way, at last became too heavy even for his powers. His friends felt anxious, but Nilson showed no anxiety; his trustful sanguine temperament, which, throughout his lifetime made him look upon every event from its hopeful side and upon every man from the best side of his character, obscured from his eyes the approach of death, and let the forebodings which inevitably precede it pass by unheeded. He was spared from long lingering and suffering. There was a sudden blow, a short struggle, and all was over.

### CXXIII.—*Degradation of Glycollic Aldehyde.*

By HENRY J. HORSTMAN FENTON, M.A., F.R.S.

By the method which has previously been described (Trans., 1895, 67, 774; 1899, 75, 575), it is easy to obtain glycollic aldehyde in a pure state, and having regard to the important position occupied by this substance as the first member of the sugar group, it appears desirable thoroughly to investigate its relationships and properties. Experiments with this object are now in progress, and the present communication gives an account of an investigation made with the view of ascertaining whether the aldehyde could be 'degraded' by the two



well-known methods which have been so successfully applied in the case of some of the higher sugars.\*

The systematic degradation of members of the sugar group can now be effected by two distinct methods, the first being that of Wohl, who obtained *d*-arabinose from *d*-glucose (*Ber.*, 1893, 26, 740), and, later, *l*-erythrose from *l*-arabinose (*Ber.*, 1899, 32, 3666). The sugar is treated with free hydroxylamine in alcoholic solution and the resulting oxime acted upon by acetic anhydride in presence of sodium acetate. In this way, the nitrile of the corresponding acid results, and all the hydroxyl groups become acetylated; glucosoxime, for example, yields the nitrile of pentacetylgluconic acid, and arabinosoxime gives the nitrile of tetracetylgluconic acid. These products readily lose hydrogen cyanide by the action of alkalis or silver oxide, yielding a derivative of the lower sugar. When pentacetylgluconic nitrile, for instance, is treated with ammoniacal silver oxide, silver cyanide separates, and an acetamide compound of the pentose results which yields the latter substance on treatment with sulphuric acid.

This method has been employed with excellent results by other chemists; Fischer, for example, degraded rhamnose to methyltetrose (*Ber.*, 1896, 29, 1380) and Maquenne (*Bull. Soc. Chim.*, 1900, 23, 587) obtained, in a similar way, *l*-erythrose from xylose.

The second method is based upon an application of the author's process of oxidation in presence of iron. In previous communications to the Society (*Trans.*, 1894, 65, 899; 1895, 67, 574; 1896, 69, 546) it has been shown that tartaric acid—which may be regarded as a normal oxidation product of tetrose—when oxidised in this way, in the cold, gives dihydroxymaleic acid, and that the latter, on heating to 50–60°, yields glycollic aldehyde.† The degradation is thus carried over two stages—tetrose to diose. In a similar way, it is hoped that tetrose may be obtained from mucic or saccharic acids, and triose from trihydroxyglutaric acid, and experiments are being made in this direction.

Ruff (*Ber.*, 1898, 31, 1573; 1899, 32, 550; 1900, 33, 3672, &c.) has applied this method with much success to the monobasic acids, and has obtained, for example, *d*-arabinose from *d*-gluconic acid, and *d*-erythrose from *d*-arabonic acid, the degradation taking place through a single stage (that is, by the removal of one carbon atom). In the first named instance, a ketonic acid appears to be the first product, so

\* The converse operation, that is, the aldol condensation of formaldehyde to glycollic aldehyde, has been effected by Pechmann (*Ber.*, 1897, 30, 2459).

† A similar result may, of course, be effected in one operation, since tartaric acid, when oxidised in presence of iron at the ordinary temperature and subsequently heated to 50–60°, yields glycollic aldehyde, but as a method of preparation, this process is less convenient owing to the necessity of separating the unaltered tartaric acid.

that in these reactions, as in the case of tartaric acid, the elimination of carbon dioxide is probably preceded by the formation of a direct oxidation product. There is, however, an important difference to be noticed in Ruff's mode of applying the oxidation process, in that he employs a *ferric* in place of a ferrous salt. In the large number of substances whose behaviour on oxidation, in presence of iron, has been studied by the author, it has invariably been found\* that a *ferrous* salt is absolutely essential and that *ferric* salts are inert. In the author's opinion, it is probable that a previous reduction of a portion of the iron first takes place in the experiments as conducted by Ruff, that is, at a more elevated temperature (the author's experiments have nearly all been made near 0°, whereas Ruff usually employs a temperature of 40°).

It is stated by Gerhard Ollendorff (*Inaugural Dissertation, Berlin*, July, 1900, 21), that glycollic acid yields formaldehyde when oxidised by hydrogen dioxide in presence of iron salts. H. O. Jones and the author have already studied the oxidation of this acid under these circumstances in the cold and have shown (*Trans.*, 1900, 77, 70) that glyoxylic acid results, so that the latter would appear to be the intermediate stage in the 'degradation' by this method. In consequence of the advent of other workers in this direction, the author confines himself in the present communication to the degradation of glycollic aldehyde by Wohl's reaction.

An alcoholic solution of glycollic aldehyde was mixed with rather more than the calculated quantity of free hydroxylamine, also in alcoholic solution, the latter being prepared according to the instructions given by Wohl (*Ber.*, 1893, 26, 730). After leaving the mixture to stand for some days, it was allowed to evaporate in a vacuum desiccator over sulphuric acid, the product being a thick syrup which refused to crystallise. Heating the mixture to 100°, prolonged standing, stirring, treatment with solvents, &c., failed to yield a crystalline product, and from the appearance and some of the properties of the syrup it was at first thought that no reaction had taken place. On analysis, however, the substance was found to contain nitrogen ( $N = 15.8$  per cent., the calculated amount being 18.6 per cent.), and subsequent experiments showed that the oxime had been formed in considerable quantity. It would appear, therefore, that the action is limited, and that some glycollic aldehyde remains unchanged. It was evident, however, that for the present object the isolation of the oxime in a pure state was not absolutely necessary, since any unaltered glycollic aldehyde would be removed by the mode of treat-

\* Except in the case of phenol, where a ferric salt appears to be as efficient as a ferrous salt, but this would appear to be undoubtedly due to previous reduction of the ferric salt, a change which can be easily demonstrated.

ment suggested. The syrup was therefore mixed with excess of acetic anhydride, together with a little fused sodium acetate, when a very violent action took place. When this had ceased, the mixture was heated for a short time on a water-bath, poured into cold water, partially neutralised with sodium carbonate, extracted several times with ether, and the ethereal solution well dried over calcium chloride. After distilling off the ether, the residual liquid was submitted to fractional distillation under reduced pressure, and the portion which came over at 100—120° under a pressure of 38 mm. was collected apart. The greater portion of this boiled under atmospheric pressure at 177—179° with, however, a considerable darkening of the liquid. The colourless distillate which came over at this temperature had a pungent odour, and was sparingly soluble in water. On analysis, the following result was obtained :

0.1614 gave 18.8 c.c. nitrogen at 18° and 745 mm.  $N = 13.36$  per cent.

When heated for a minute or two with aqueous sodium hydroxide, it turned yellow, and the product on acidification gave a strong odour of hydrocyanic acid ; tested with iron salts, it gave an intense Prussian blue reaction. This product is evidently, as might be expected from the general type of Wohl's reaction, the acetyl derivative of glycollic nitrile (or acetoxyacetonitrile),  $\text{CH}_3 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CN}$ , which requires  $N = 14.14$  per cent. The last-named compound was obtained by Henry from the halogen derivatives of acetonitrile (*Compt. rend.*, 1886, 102, 769 ; 103, 413) and from the union of hydrogen cyanide with formaldehyde and subsequent acetylation with acetic anhydride (*Compt. rend.*, 1890, 110, 759), and is described as a colourless liquid boiling at 177° (an analysis is not given).

When this nitrile was dissolved in alcohol and mixed in the cold with the calculated quantity of silver oxide dissolved in aqueous ammonia, a separation began, almost immediately, of silver cyanide in a beautifully crystalline condition, a slight reduction of the silver taking place at the same time. After the mixture had been allowed to stand for about twenty-four hours, it was filtered, the liquid allowed to evaporate to a syrup in a vacuum desiccator, taken up with alcohol, again filtered and evaporated as before. The resulting product, which was partly syrupy and partly crystalline, gave the characteristic odour of formaldehyde when heated with moderately dilute sulphuric acid ; for further identification, the vapours were collected in a small quantity of ice-cold water and examined as follows :

1. Ammoniacal silver nitrate gave a silver mirror after standing for a few minutes.
2. A rosaniline salt, which had been bleached by sulphurous acid, gave, almost immediately, a bright magenta colour.

3. Heated with resorcinol and strong soda solution, a red colour was obtained.

4. The solution was saturated with hydrogen sulphide, and allowed to stand for several hours; the resulting mixture, which had an alliaceous odour, was heated to boiling with half its volume of concentrated hydrochloric acid, and allowed to stand, when silky needles of trithioformaldehyde separated, which melted at about  $210^{\circ}$ .

5. By the action of phenylhydrazine. Phenylhydrazine acetate gave a bulky, flocculent, pale yellowish-white precipitate, which was collected, washed with absolute alcohol, and then three times with boiling ether, and was afterwards recrystallised from a mixture of toluene and absolute alcohol. It was thus obtained in the form of lustrous rhombic tablets, which melted sharply at  $181^{\circ}$ . (Compare Wallace Walker, Trans., 1896, 69, 1278).

The identity of the product is, in fact, beyond all doubt, and its properties form a striking contrast to those of glycollic aldehyde as regards odour, much greater volatility, and the reactions 4 and 5 above mentioned.

The degradation of glycollic aldehyde by this method is therefore extremely simple and evidently takes place in a perfectly normal manner.

The nature of the intermediate product which is formed by the action of ammoniacal silver oxide on the nitrile has not yet been studied owing to the small amount of material available. Presumably it is either hexamethyleneamine or, more probably, an acetamide compound of formaldehyde analogous to the products obtained by Wohl in the case of the higher sugars.

Most of the materials necessary for this investigation were provided by the funds placed at the author's disposal by the Government Grant Committee of the Royal Society.

#### CXXIV.—*Researches on the Alkyl-substituted Succinic Acids. Part III. Dissociation Constants.*

By WILLIAM A. BONE and CHARLES H. G. SPRANKLING.

In our last communication (this vol., 654), we showed that the two isopropyl groups in *cis*-s-diisopropylsuccinic acid have an extraordinary influence upon its dissociation constant, and in discussing the constants of alkyl-substituted succinic acids as a class, we ex-

pressed the opinion that the data then available were not sufficient to justify our making any very definite statement as to the factors which determine the magnitudes of the constants in this particular series. The experiments recorded in the present paper, we hope, will go some way towards supplying this deficiency, and, together with previous results, will provide an adequate basis of fact for the discussion of a very difficult question.

In the first place, it seemed desirable to ascertain whether other 'iso' groupings have an influence upon the dissociation constant of a succinic acid in any way comparable with that of the two *isopropyl* groups in *cis-s*-diisopropylsuccinic acid. We therefore investigated the hitherto unknown *s*-diisobutylsuccinic acids from this standpoint, and also determined the constants of several new  $\alpha\alpha_1$ -dialkyl- and trialkyl-succinic acids which seemed likely to afford evidence directly bearing on the question at issue. A full discussion of these and previous results will be found at the end of the paper.

#### A. *s*-Diisobutylsuccinic Acids.

The preparation of these acids involved the following operations :

- (1.) The preparation of *isobutylacetic* acid from ethyl malonate and *isobutyl* bromide,
- (2.) The bromination of *isobutylacetic* acid by the Hell-Volhard-Zelinsky method,
- (3.) The preparation of ethyl  $\beta$ -*isobutylcyanosuccinate* by the interaction of ethyl  $\alpha$ -bromo*isobutylacetate* and the sodium derivative of ethyl cyanoacetate,
- (4.) The *isobutylation* of ethyl  $\beta$ -*isobutylcyanosuccinate*, and the subsequent hydrolysis of the ethyl  $\alpha\beta$ -di*isobutylcyanosuccinate* so obtained.

We will briefly describe the later stages of the preparation.

*Ethyl  $\beta$ -isobutylcyanosuccinate* was obtained by heating an alcoholic solution of the sodium derivative of ethylecyanoacetate with the calculated quantity of ethyl  $\alpha$ -bromo*isobutylacetate* in soda-water bottles to 100° for 24 hours, the details being similar to those given for the preparation of ethyl  $\beta\beta$ -dimethylcyanosuccinate (Trans., 1899, 75, 854). The yield of refractionated oil was 65 per cent. of that theoretically possible, it was nearly colourless, had a density  $d_{0^\circ/4^\circ}$  1.0455, and a refractive index  $\mu_{Na}$  1.4408. On analysis:

0.1902 gave 0.4253 CO<sub>2</sub> and 0.1439 H<sub>2</sub>O. C = 60.99 ; H = 8.41.

0.2926 „ 14.15 c.c. nitrogen at 14° and 746 mm. N = 5.71.

C<sub>13</sub>H<sub>21</sub>O<sub>4</sub>N requires C = 61.17 ; H = 8.23 ; N = 5.59 per cent.

In order to prove the constitution of the oil, a portion of it was

hydrolysed with concentrated hydrochloric acid, when an acid melting at  $107^{\circ}$ , and in all other respects identical with isobutylsuccinic acid, was obtained. The acid was analysed with the following results:

0.2021 gave 0.4085  $\text{CO}_2$  and 0.1490  $\text{H}_2\text{O}$ .  $\text{C}=55.11$ ;  $\text{H}=8.19$ .

0.1329 of the silver salt gave on ignition 0.0739 Ag.  $\text{Ag}=55.59$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C}=55.17$ ;  $\text{H}=8.04$  per cent.

$\text{C}_8\text{H}_{12}\text{O}_4\text{Ag}_2$  „  $\text{Ag}=55.68$  per cent.

Ethyl  $\alpha\beta$ -diisobutylcyanosuccinate was prepared by heating molecular proportions of the sodium derivative of ethyl  $\beta$ -isobutylcyanosuccinate and isobutyl bromide with alcohol in soda-water bottles at  $100^{\circ}$  for 24 hours. As the liquid still remained alkaline, more isobutyl bromide was added and the process continued for a second period of 24 hours. The product, isolated in the usual manner, was twice fractionated under reduced pressure.

The refractionated oil was very viscous and nearly colourless; it boiled at  $187$ — $189^{\circ}$  under 20 mm. pressure, had a density  $d_{0^{\circ}/4^{\circ}} 1.0128$ , and a refractive index  $\mu_{\text{Na}} 1.4462$ . On analysis:

0.2103 gave 0.5036  $\text{CO}_2$  and 0.1790  $\text{H}_2\text{O}$ .  $\text{C}=65.31$ ;  $\text{H}=9.46$ .

0.2199 „ 8.7 c.c. nitrogen at  $21^{\circ}$  and 754 mm.  $\text{N}=4.69$ .

$\text{C}_{17}\text{H}_{29}\text{O}_4\text{N}$  requires  $\text{C}=65.59$ ;  $\text{H}=9.32$ ;  $\text{N}=4.50$  per cent.

The oil was hydrolysed in two stages, namely, first with alcoholic potash (1 hour) in order to obtain the  $\alpha\beta$ -diisobutylcyanosuccinic acid, which was then boiled for 36 hours with 50 per cent. sulphuric acid on the sand-bath (compare this vol., 659). Oily particles of the anhydride of *cis*-diisobutylsuccinic acid separated out during the process, and on cooling crystals of the *trans*-isomeride appeared in the liquid. The whole was at once submitted to steam distillation, when the *cis*-anhydride passed over as a colourless oil, leaving the *trans*-acid behind; the separation of the two isomerides was complete. The *cis*-acid was obtained from the aqueous distillate, and the *trans*-acid from the residual liquid exactly as described in our previous paper (*loc. cit.*, 661).

*cis*-s-Diisobutylsuccinic acid is very sparingly soluble in water, and after two or three recrystallisations from that solvent melts at  $97$ — $98^{\circ}$ . On analysis:

0.1935 gave 0.4419  $\text{CO}_2$  and 0.1633  $\text{H}_2\text{O}$ .  $\text{C}=62.30$ ;  $\text{H}=9.38$ .

0.1867 of the silver salt gave on ignition 0.0907 Ag.  $\text{Ag}=48.57$ .

$\text{C}_{12}\text{H}_{22}\text{O}_4$  requires  $\text{C}=62.60$ ;  $\text{H}=9.56$  per cent.

$\text{C}_{12}\text{H}_{20}\text{O}_4\text{Ag}_2$  „  $\text{Ag}=48.66$  per cent.

The anhydride of this acid, obtained in the usual manner, was a colourless oil boiling at  $280$ — $286^{\circ}$  under atmospheric pressure;

with aniline, it yielded a *liquid* anilic acid, resembling in this particular *cis-s*-diisopropylsuccinic acid. The sparingly soluble calcium salt had the composition  $C_{12}H_{20}O_4Ca, 3H_2O$ .

*trans-s-Diisobutylsuccinic Acid*.—The crude acid obtained on extracting the residual liquor in the distillation flask melted at  $170-180^\circ$ , but after two or three recrystallisations from a mixture of benzene and light petroleum it melted at  $193-195^\circ$ . That it was now quite free from the *cis*-isomeride was shown by the fact that treatment with cold acetyl chloride had no effect on its melting point. On analysis:

0.1516 gave 0.3475  $CO_2$  and 0.1356  $H_2O$ .  $C = 62.49$ ;  $H = 9.94$ .

0.2020 of the silver salt gave on ignition 0.0982 Ag.  $Ag = 48.61$ .

$C_{12}H_{22}O_4$  requires  $C = 62.60$ ;  $H = 9.56$  per cent.

$C_{12}H_{20}O_4Ag_2$  „  $Ag = 48.66$  per cent.

The acid dissolves on being heated with acetyl chloride, forming a liquid anhydride which, with water, yields the original acid again, and with aniline, a *solid* anilic acid melting at  $134-135^\circ$ .

*Conversion of the trans- into the cis-Acid*.—The *trans*-acid is quantitatively converted into the *cis*-isomeride by heating it in a sealed tube with acetyl chloride or acetic anhydride at  $180^\circ$ , and subsequently converting the *cis*-anhydride so formed into the acid.

On the other hand, we have not been able to effect even a partial conversion of the *cis*- into the *trans*-acid, although we heated it in a sealed tube with concentrated hydrochloric acid at  $230^\circ$  for 24 hours. *cis-s*-Diisopropylsuccinic acid, we have shown, undergoes no alteration on being heated with hydrochloric acid to  $180^\circ$ , but at  $220-230^\circ$  is to a very small extent converted into the *trans*-form. Evidently *cis-s*-diisobutylsuccinic acid is a still more stable substance.

*Dissociation Constants*.\*—The *s*-diisobutylsuccinic acids are so sparingly soluble in water that in neither case were we able to obtain a solution containing the gram-molecule in less than 600 litres. It was therefore necessary to apply a correction for the resistance of the water in each case. The following are the corrected values obtained:

*cis-s-Diisobutylsuccinic acid.*

$v$ .	$\mu_m$	$m$ .	100 <i>k</i> .
668.5	157.0	0.4510	0.0555
1337.0	198.0	0.5648	0.0548
2674.0	241.5	0.6900	0.0574

$$K = 0.056.$$

\* The determinations of these and all other dissociation constants included in this and our two previous papers were made at a temperature of  $25^\circ$ .

*trans-s-Diisobutylsuccinic acid.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
1060	134.5	0.3843	0.0226
2120	172.2	0.4920	0.0224
4240	214.5	0.6135	0.0232

$$K = 0.0225.$$

These numbers indicate that the two isobutyl groups have no such extraordinary influence on the constant of a succinic acid as the two isopropyl groups have in the case of *cis-s-isopropylsuccinic acid*.

*B.  $\alpha_1$ -Methylpropylsuccinic Acids.*

*Ethyl  $\beta$ -methyl- $\alpha$ -propylcyanosuccinate* was prepared by heating an alcoholic solution of the sodium compound of ethyl  $\beta$ -methylcyanosuccinate (compare Trans., 1899, 75, 853) with the calculated quantity of propyl iodide on the water-bath in a reflux apparatus until the liquid became neutral (45 mins.). The propylated oil was extracted as usual and twice refractionated. The yield was 81 per cent. of that theoretically possible. The oil boiled at 169—171° under 24 mm. pressure, had a density  $d_{0^\circ/4^\circ}$  1.0501 and a refractive index  $\mu_{Na}$  1.4428. On analysis:

0.2077 gave 0.4647 CO<sub>2</sub> and 0.1591 H<sub>2</sub>O. C = 61.01; H = 8.51.

0.3122 „ 15.3 c.c. nitrogen at 19° and 766 mm. N = 5.68.

C<sub>18</sub>H<sub>21</sub>O<sub>4</sub>N requires C = 61.17; H = 8.23; N = 5.59 per cent.

It was hydrolysed in two stages and the resulting *cis*- and *trans*- $\alpha_1$ -methylpropylsuccinic acids were separated by steam distillation as described in the preceeding section of this paper.

*cis*- $\alpha_1$ -Methylpropylsuccinic acid is fairly soluble in water and is best recrystallised from warm benzene. It melts at 92—93°. On analysis:

0.1726 gave 0.3486 CO<sub>2</sub> and 0.1269 H<sub>2</sub>O. C = 55.09; H = 8.17.

0.1163 of the silver salt on ignition gave 0.0648 Ag. Ag = 55.70.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.17; H = 8.04 per cent.

C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>Ag<sub>2</sub> „ Ag = 55.68 per cent.

The acid gave a liquid anhydride which, with aniline, yielded an anilic acid melting at 82—84°.

*trans*- $\alpha_1$ -Methylpropylsuccinic acid is less soluble in water than the *cis*-isomeride, and after two or three recrystallisations from a mixture of benzene and light petroleum, melts at 158—160°. On analysis:

0.2219 gave 0.4477 CO<sub>2</sub> and 0.1659 H<sub>2</sub>O. C = 55.02; H = 8.26.

0.1972 of the silver salt on ignition gave 0.1100 Ag. Ag = 55.78.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.17; H = 8.04 per cent.

C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>Ag<sub>2</sub> „ Ag = 55.68 per cent.



The acid gradually dissolved in warm acetyl chloride forming a liquid anhydride which with water yielded the original acid again, and with aniline an anilic acid melting at 166—167°.

*Mutual Conversion of cis- and trans-Acids.*—(1) On heating the *cis*-acid in a sealed tube with strong hydrochloric acid for 8 hours, a partial conversion into the *trans*-isomeride occurred. The resulting mixture melted indefinitely between 130° and 150°, and was subsequently resolved into two portions melting at 92° and 156—158° respectively.

(2) The *trans*-acid was quantitatively converted into the *cis*-anhydride on being heated in a sealed tube with acetic anhydride to 180° for 6 hours.

*Dissociation constants.*—The following are the values obtained :

*cis-aa<sub>1</sub>-Methylpropylsuccinic acid.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
26.5	28.39	0.0811	0.0270
53.0	39.18	0.1119	0.0267
106.0	53.31	0.1560	0.0272
212.0	74.70	0.2135	0.0273

$$K = 0.0271.$$

*trans-aa<sub>1</sub>-Methylpropylsuccinic acid.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
55.0	44.42	0.1272	0.0336
110.0	61.04	0.1774	0.0334
220.0	82.03	0.2344	0.0333
440.0	110.3	0.3152	0.0330

$$K = 0.0335.$$

*C. aa<sub>1</sub>-Methylisobutylsuccinic Acids.*

The preparation of these acids from ethyl  $\beta$ -methylcyanosuccinate is so similar to that of the acids already described, that it is hardly necessary for us to give any detailed account of it.

*Ethyl  $\beta$ -methyl- $\alpha$ -isobutylcyanosuccinate* is a colourless oil boiling at 186—188° under 35 mm. pressure, having a density  $d_{0^\circ/4^\circ}$  1.0528 and a refractive index  $\mu_{Na}$  1.4446.

The two isomeric methylisobutylsuccinic acids obtained on hydrolysing this oil have properties so similar to those of the acids described in the preceding section that we may simply tabulate them as follows :

	M. p. .		M. p.
	<i>Acid.</i>	<i>Anhydride.</i>	<i>Anilic acid.</i>
<i>trans-aa<sub>1</sub>-Methylisobutylsuccinic ...</i>	133°	liquid	132—133
<i>cis    "                                "                                "                                "</i>	88—90°	"	94—96°

*Dissociation constants.*—The following are the values obtained :

*cis- $\alpha\alpha_1$ -Methylisobutylsuccinic acid.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100%.
34.5	40.08	0.1145	0.0429
69.0	55.73	0.1592	0.0427
138.0	75.18	0.2148	0.0426
276.0	101.0	0.2885	0.0424

$$K = 0.0427.$$

*trans- $\alpha\alpha_1$ -Methylisobutylsuccinic acid.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100%.
88.9	47.28	0.1351	0.0237
177.8	64.43	0.1841	0.0234
355.6	87.45	0.2498	0.0234
711.2	116.10	0.3318	0.0233

$$K = 0.0236.$$

*D.  $\alpha\alpha_1$ -Methylisoamylsuccinic Acids.*

Dr. Lawrence kindly furnished us with specimens of the *cis*- and *trans- $\alpha\alpha_1$* -methylisoamylsuccinic acids described in a recent communication to the Society (Proc., 1899, 15, 163); we obtained the following results for their dissociation constants.

*cis-Acid, m. p. 93°.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100%.
52.3	46.31	0.1323	0.0385
104.6	63.36	0.1810	0.0382
209.2	86.45	0.2470	0.0387
418.4	114.98	0.3284	0.0385

$$K = 0.0385.$$

*trans-Acid, m. p. 141—142°.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100%.
183.4	65.61	0.1875	0.0236
366.8	87.69	0.2535	0.0234
733.6	118.70	0.3393	0.0238
1467.2	154.7	0.4429	0.0240

$$K = 0.0236.$$

*E. Trialkyl-substituted Succinic Acids.*

Since we are now able to prepare ethyl  $\beta\beta$ -dimethylcyanosuccinate in large quantities, and as the introduction of a third alkyl radicle into this molecule is an easy matter, we have been able to investigate

a large number of trialkylsuccinic acids containing two methyl and a third variable radicle. Of these, we prepared the dimethylethyl-, dimethylpropyl-, dimethylisopropyl-, and the dimethylisoamyl-succinic acids, whilst Dr. Lawrence kindly gave us a specimen of dimethylisobutyl-succinic acid.

The details of the preparation of these acids from ethyl  $\beta\beta$ -dimethylcyanosuccinate are so similar to those described under trimethylsuccinic acid in a previous paper (Trans., 1899, 75, 855), that we need not give them; the yields of trialkylated cyanosuccinic esters usually amounted to about 80 per cent. of those theoretically possible. Each oil was hydrolysed by boiling it with excess of strong hydrochloric acid in a reflux apparatus until the whole of it had dissolved. The time required for the process varied with the mass and character of the third alkyl radicle introduced. Thus, whilst ethyl  $\beta\beta$ -dimethylcyanosuccinate required only 15 hours for complete hydrolysis with strong hydrochloric acid, the trimethyl ester required 40 hours, the dimethylethyl 48 hours, the dimethylpropyl 84 hours, the dimethylisopropyl 96 hours, and the dimethylisoamyl 144 hours under the same conditions. On cooling the liquid in each case, almost the whole of the acid separated as a white, crystalline powder which was afterwards purified by repeated recrystallisation either from strong hydrochloric acid or hot benzene. The only impurity likely to survive this treatment would be a small quantity of *as*-dimethylsuccinic acid resulting from any unchanged ethyl  $\beta\beta$ -dimethylcyanosuccinate in the oil hydrolysed; analyses of the acids and their silver salts, however, showed that in no case was it present.\*

*aa*-Dimethyl- $\alpha_1$ -ethylsuccinic acid melted at 139–140°. On analysis:

0.1826 gave 0.3684  $\text{CO}_2$  and 0.1349  $\text{H}_2\text{O}$ .  $\text{C}=55.0$ ;  $\text{H}=8.21$ .

0.2109 of the silver salt gave on ignition 0.1169 Ag.  $\text{Ag}=55.44$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C}=55.17$ ;  $\text{H}=8.05$  per cent.

$\text{C}_8\text{H}_{12}\text{O}_4\text{Ag}_2$  „  $\text{Ag}=56.68$  per cent.

#### Dissociation constant.

$v$ .	$\mu_{90}$ .	$m$ .	100%.
59.2	58.34	0.1667	0.0563
118.4	79.63	0.2275	0.0566
236.8	107.20	0.3063	0.0571
473.6	140.8	0.4023	0.0572

$$K = 0.0566.$$

*aa*-Dimethyl- $\alpha_1$ -propylsuccinic acid melted at 145°. On analysis:

\* *as*-Dimethylsuccinic acid,  $\text{C}_6\text{H}_{10}\text{O}_4$ , contains  $\text{C}=49.31$ ,  $\text{H}=6.81$  per cent. and its silver salt contains  $\text{Ag}=60.00$  per cent.

0.2144 gave 0.4512 CO<sub>2</sub> and 0.1671 H<sub>2</sub>O. C=57.40; H=8.66.

0.2966 of the silver salt gave on ignition 0.1594 Ag. Ag=53.72.

C<sub>9</sub>H<sub>16</sub>O<sub>3</sub> requires C=57.46; H=8.51 per cent.

C<sub>9</sub>H<sub>14</sub>O<sub>4</sub>Ag<sub>2</sub> „ Ag=53.99 per cent.

This acid also gave a liquid anhydride and an anilic acid melting at 166—167°.

*Dissociation constant.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
108.5	78.68	0.2248	0.0601
217.0	105.40	0.3011	0.0598
434.0	138.50	0.3956	0.0596
868.0	176.50	0.5042	0.0591

$$K=0.060.$$

*αα*-Dimethyl-*α*-1-isopropylsuccinic acid melted at 141—142°. On analysis:

0.2072 gave 0.4355 CO<sub>2</sub> and 0.1620 H<sub>2</sub>O. C=57.31; H=8.69.

0.3172 of the silver salt gave 0.1680 Ag. Ag=53.69.

C<sub>9</sub>H<sub>16</sub>O<sub>4</sub> requires C=57.46; H=8.51 per cent.

C<sub>9</sub>H<sub>14</sub>O<sub>4</sub>Ag<sub>2</sub> „ Ag=53.99 per cent.

The acid forms a liquid anhydride, and an anilic acid melting at 197—199°.

*Dissociation constant.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
66.1	35.66	0.1019	0.0159
132.2	46.96	0.1342	0.0157
264.4	63.01	0.1800	0.0150
528.8	85.06	0.2430	0.0148

$$K=0.0158.$$

*αα*-Dimethyl-*α*-1-isobutylsuccinic Acid.—Specimen prepared by Dr. Lawrence. Melting point 143—144°.

*Dissociation constant.*

<i>v.</i>	$\mu_v$	<i>m.</i>	100 <i>k.</i>
273.0	101.4	0.2898	0.0434
546.0	123.3	0.3810	0.0429
1092.0	171.5	0.4900	0.0431
2184.0	223.9	0.6083	0.0432

$$K=0.0432.$$

*αα*-Dimethyl-*α*-1-isocamylsuccinic acid melted at 143—144°. On

0.2126 gave 0.4701  $\text{CO}_2$  and 0.1781  $\text{H}_2\text{O}$ .  $\text{C} = 60.31$ ;  $\text{H} = 9.31$ .  
 0.1926 of the silver salt gave on ignition 0.0965 Ag.  $\text{Ag} = 50.1$ .

$\text{C}_{11}\text{H}_{20}\text{O}_4$  requires  $\text{C} = 60.54$ ;  $\text{H} = 9.17$  per cent.

$\text{C}_{11}\text{H}_{18}\text{O}_4\text{Ag}_2$  „  $\text{Ag} = 50.0$  per cent.

#### *Dissociation constant.*

<i>v.</i>	$\mu_{\text{H}}$	<i>m.</i>	100 <i>k.</i>
121.2	83.43	0.2384	0.0616
242.4	111.60	0.3189	0.0616
484.8	145.50	0.4157	0.0610
969.6	184.20	0.5263	0.0603

$$K = 0.0616.$$

#### *Discussion of Results.*

The dissociation constants of a very large number of alkyl-substituted succinic acids have now been determined; in no other series of acids are the data available for a discussion of the connection between the chemical constitution and this characteristic physical constant so complete.

On *a priori* grounds, we should conclude that the value of the constant in this series would be largely influenced by the following factors: (1) The number of the substituting alkyl groups; (2) their mass and chemical structure; (3) the mutual influence of the two carboxyl groups, largely dependent on the distance between them.

With regard to the third factor, it is obvious that the mutual effect of the two carboxyl groups in the molecule must increase the tendency to ionisation in aqueous solution. As an extreme instance of this effect, we might quote the constant of malonic acid (0.163), which is ninety times as great as that of acetic acid (0.0018). The magnitude of this mutual reinforcement will vary inversely as the distance between the two groups in question, and as there is good reason for believing that in the alkylsuccinic acids this distance decreases with the number of the substituting radicles, we must endeavour to distinguish between the *direct* effect of successive substitutions and the accompanying *indirect* effect due to the approximation of the two carboxyl groups.

It has been argued that because the direct observed effect of successive methyl substitutions in the acetic acid series is to lower the value of the constant, it must necessarily be so in every other series, (compare Walker, this vol., 397) but this contention is based on purely empirical evidence, and is unsupported by any *a priori* consideration.

It remains now to see how far we can trace the effects of these

different factors in the succinic series. In the first place, so far as our experience of anhydride formation in this series goes, we are inclined to think that the relative distances of the two carboxyl groups in members containing the *same* number of alkyl radicles are practically equal, for we have never been able to detect any difference in the tendencies to anhydride formation in such cases, although we have examined a large number of them. Hence differences in their dissociation constants may be ascribed to the influence of the second factor, namely, mass or chemical structure of the substitution alkyls.

On tabulating the values for mono-substituted succinic acids determined by ourselves and others as follows :

Monomethyl.....	0.0085	Monoisopropyl .....	0.0076
Monoethyl .....	0.0085	Monoisobutyl .....	0.0088
Monopropyl .....	0.00886	Monoisoamyl .....	0.0096

we observe that an increase in the mass of the alkyl radicle is accompanied by a tendency to increase in the constant, except in the case of the *isopropyl* group, which clearly exerts a lowering influence.

If the values of the  $\alpha\alpha_1$ -dialkyl acids containing one methyl and a second variable radicle be compared as follows :

	<i>Trans.</i>	<i>Cis.</i>
<i>s</i> -Dimethyl .....	0.0196	0.0123
$\alpha\alpha_1$ -Methylethyl .....	0.0207	0.0201
$\alpha\alpha_1$ -Methylpropyl.....	0.0335	0.0271
$\alpha\alpha_1$ -Methylisopropyl.....	0.0158	0.066
$\alpha\alpha_1$ -Methylisobutyl .....	0.0226	0.056
$\alpha\alpha_1$ -Methylisoamyl .....	0.0236	0.0385

it will be seen that so long as the variable radicle remains *normal* the constant increases with its mass in both the *cis*- and *trans*-series. As soon, however, as the variable radicle contains an '*iso*' grouping we find a 'lowering' effect in the *trans*-series, and a very marked 'raising' effect in the *cis*-series, and both these opposite effects are the more marked the nearer the peculiar grouping of the carbon atoms in the *iso*-radicle is to the carbon atom to which the carboxyl group is attached. Further, it is rather a remarkable coincidence that only in the case of acids where the second variable radicle is normal are the constants of the *trans*-acids greater than those of the corresponding *cis*-isomerides.

Similar effects are to be observed in the case of trialkyl acids containing two methyl groups attached to the one carbon atom and a third variable radicle to the other carbon atom, thus

Trimethyl.....	0.0320	Dimethylisopropyl .....	0.0150
Dimethylethyl .....	0.0566	Dimethylisobutyl .....	0.0432
Dimethylpropyl .....	0.0600	Dimethylisoamyl .....	0.0210

Here, again, so long as the variable radicle remains *normal* an increase in its mass is accompanied by a marked increase in the constant, but this 'mass' influence is masked by the opposite effect of the '*iso*' structure in the last three acids, and, again, the magnitude of this structural effect depends on the proximity of the '*iso*' linking to the carbon to which the carboxyl group is attached.

We will now tabulate those symmetrically substituted dialkylsuccinic acids whose constants have been determined.

	<i>Trans.</i>	<i>Cis.</i>
<i>s</i> -Dimethyl .....	0.0196	0.0123
<i>s</i> -Diethyl .....	0.0245	0.0201
<i>s</i> -Dipropyl .....	0.0250	0.049
<i>s</i> -Diisopropyl .....	0.0108	0.230
<i>s</i> -Diisobutyl .....	0.0226	0.056

Again, we find that so long as the two alkyl radicles have a normal structure, the value of the constant increases with their masses in both the *cis*- and *trans*-series. On the other hand, just as in the case of the  $\alpha_1$ -acids when the alkyl groups have an '*iso*' structure, we observe a 'lowering' effect in the *trans*-series and a 'raising' effect in the corresponding *cis*-series, these 'structural' effects being again most marked in the two diisopropyl acids.

The conclusion may therefore be drawn that in this series of acids each alkyl group exerts its own influence upon the dissociation constant dependent upon its mass and structure. In the case of *normal* radicles, we have simply the effect of 'mass' to consider, an increase in the mass of a variable radicle invariably raises the constant. The 'structural' effect in case of *iso*-radicles is opposed to that of mass, except in the case of *cis*-symmetrically substituted dialkyl acids, and its magnitude always depends on the proximity of the '*iso*' linking to the carbon atom to which the carboxyl group is attached.

We have in our previous paper discussed the effects, direct or indirect, of successive alkyl substitutions on the constant of succinic acid. There can be no doubt as to the observed effects, for the constant of every monoalkylsuccinic acid is greater than that of succinic acid, those of the  $\alpha_1$ -dialkyl acids are all greater than the highest value observed in the case of the monoalkyl series, and those of the trialkyl acids we have studied are all greater than that of the *as*-dimethylsuccinic acid from which they are derived. Whether this general effect is direct or indirect is a matter of opinion, but if we consider it indirect, and due to the greater proximity of the two carboxyl groups, we have still further to explain why the constant of *cis-s*-diisopropylsuccinic acid is so many times greater than that of any other

*cis-s*-dialkyl acid, although there are no appreciable differences in their tendencies to anhydride formation.

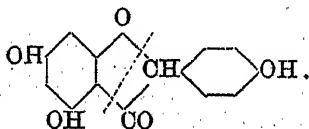
We have pleasure in stating that the greater part of the cost of the materials used in this investigation was defrayed by grants from the Research Fund of the Chemical Society.

THE OWENS COLLEGE,  
MANCHESTER.

### CXXV.—*Genistein. Part II.*

By ARTHUR GEORGE PERKIN, F.R.S.E., and LOUIS HUBERT HORSFALL.

It was shown (Trans., 1899, '75, 830) that dyer's broom (*Genista tinctoria*) contains, in addition to luteolin, a new substance genistein, which possesses feeble dyeing properties. When decomposed, the latter gave phloroglucinol and an acid resembling *p*-hydroxyphenylacetic acid, and this reaction, together with its other properties, indicated it to be a trihydroxyphenylketocumaran.



Further investigation, however, was desirable in order to establish the identity of the acid and the nature of the products of methylation. These points could not be dealt with previously owing to the small quantity of genistein which the plant contains and the laborious nature of the operations for its extraction and complete purification. For the apparently meagre results of this paper, 25 grams of genistein were employed, the preparation of which extended throughout five months.

#### *Methylation products of Genistein.*

It has been shown (*loc. cit.*) that by methylation genistein yields two dimethyl ethers, (a) the main product melting at 137—139°, and (b) present in minute quantity and characterised by its sparing solubility in alcohol. The ether (a) was first examined.

This substance, to which the formula  $C_{14}H_8O_5(O\cdot CH_3)_2$  was assigned, was a monoacetyl compound,  $C_{14}H_7O_5(O\cdot CH_3)_2\cdot C_2H_3O$ , and that the latter had the composition assigned to it was evident from a study of its decomposition with an acid.



0.6710 dissolved in 15 c.c. of boiling acetic acid and treated with 2 c.c. of sulphuric acid gave 0.5815  $C_{16}H_{14}O_5$ .

Found 86.66 per cent. Calculated 87.19 per cent.

*Decomposition with Alcoholic Potash.*—The dimethyl ether (a) was digested with strong alcoholic potash at 150–160° for 3 hours. The resulting solution was evaporated to dryness, the residue dissolved in water, neutralised with acid, treated with excess of sodium hydrogen carbonate, and extracted with ether. On evaporation, a small quantity of colourless residue remained which did not crystallise on long standing, and was similar in character to that yielded by luteolin trimethyl ether (this vol., p. 1317) by this method. To identify it, the residue was dissolved in dilute sodium carbonate solution, diazobenzene sulphate added, and the red precipitate thus produced collected, washed, dried, and purified by extraction with alcohol and crystallisation from a mixture of alcohol and acetic acid. It formed a glistening mass of orange-red needles melting at 251–252°, did not dissolve in cold aqueous alkalis, and was identical with *disazobenzenephloroglucinol monomethyl ether*, previously prepared from the methyl ethers of quercetin (Proc., 1900, 16, 181) and luteolin. The sodium hydrogen carbonate solution from which this phenol had been removed was neutralised with acid, extracted with ether, and the extract evaporated. The resulting oily residue gradually solidified and was then digested with boiling light petroleum, filtered, and the crystals which had separated overnight recrystallised from the same solvent with the aid of animal charcoal.

0.1088 gave 0.2594  $CO_2$  and 0.0595  $H_2O$ . C = 65.02; H = 6.07.

0.1365 „ 0.1940 AgI.  $CH_3 = 9.07$ .

$C_9H_{10}O_3$  requires C = 65.06; H = 6.02;  $CH_3 = 9.03$  per cent.

This acid consisted of colourless leaflets melting at 85–86°, and was identical with the methoxyphenylacetic acid,  $CH_3 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ , prepared by Cannizzaro (*Annalen*, 1861, 117, 243). The decomposition products of genistein dimethyl ether (a) are thus *phloroglucinol monomethyl ether* and *p-methoxyphenylacetic acid*, consequently this compound is the normal dimethyl ether of the colouring matter.

*The sparingly soluble Dimethyl Ether (b).*—The yield of this product was exceedingly small and little more than one gram was available for investigation. The melting point, previously given as 187–189°, is too low, and should be 200–202°. It has been shown (*loc. cit.*) that this substance contains two methoxy-groups, and that by the action of hydriodic acid genistein or a very similar compound is formed. To account for its production, it seemed possible that during methylation a methyl group had entered the ring, the product being consequently a dimethyl ether of methylgenistein (*loc. cit.*).

The acetyl derivative prepared in the usual manner forms colourless needles, dissolves sparingly in alcohol, and melts at 212—214°. It contains only one acetyl group.

0.6548 gave 0.5768 regenerated ether. Found 88.08.

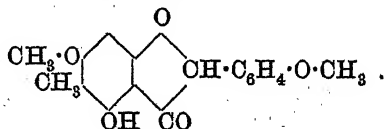
$C_{14}H_7O_3(O \cdot CH_3)_2 \cdot C_2H_5O$  requires  $C_{16}H_{14}O_5 = 87.19$  per cent.  
 $CH_3 \cdot C_{14}H_8O_3(O \cdot CH_3)_2 \cdot C_2H_5O$  „  $C_{17}H_{16}O_5 = 87.72$  „

The regenerated dimethyl ether melting at 200—202° was analysed.

0.1148 gave 0.2886  $CO_2$  and 0.0555  $H_2O$ .  $C = 68.56$ ;  $H = 5.37$ .

$C_{17}H_{16}O_5$  requires  $C = 68.00$ ;  $H = 5.33$  per cent.

By the action of alcoholic potash at 150—160°, this ether yielded an acid which crystallised in colourless leaflets, melted at 85—86°, and was identical with *p-methoxyphenylacetic acid*. The phenolic product of the decomposition became crystalline on standing, and was identical in appearance with that yielded by the analogous trimethyl ether of high melting point from luteolin (*loc. cit.*). That it was the same substance was confirmed by the preparation of its disazobenzene derivative, for this formed orange-red needles melting at 198—201°. As previously indicated, this is most probably *disazobenzenemethylphloroglucinol monomethyl ether*, and consequently the ether obtained from genistein melting at 200—202° is considered to be *methylgenistein dimethyl ether*. The following would appear to be its constitution:



To determine whether any characteristic distinction could be noted between genistein and the presumed methylgenistein, a trace of each was prepared by the decomposition of the respective methyl ethers with hydriodic acid. In appearance and general reactions, both products appeared to be identical, but a distinction in the melting point was noted, as the genistein melted at 287—289°,\* and the methylgenistein at 276—278°. From these results, it is unlikely that methylgenistein or its glucoside exists in the *Genista tinctoria*, and the substance is almost certainly produced in the form of its ether during methylation. Owing to lack of material, experiments could not be made to determine if it could be formed by digesting genistein dimethyl ether with methyl alcoholic potash and methyl

\* A sample of genistein from the dyer's broom, the purity of which could not be ascertained, melted at 291—293°, slightly higher than that from the ether, a fact easily explained, as the quantity of the latter did not admit of recrystallisation.

iodide, but by acting at first with a somewhat larger quantity of the alkali and iodide upon genistein, it was observed that the yield of the methylgenistein compound was somewhat increased. Owing to the difficulty in preparing it, we do not propose to examine it further, for its analogy to the methylluteolin ether is evident.

*Genistein Diethyl Ether.*

Genistein dissolved in a solution of potassium hydroxide (5 mols.) in ethyl alcohol was digested at the boiling point with excess of ethyl iodide for 3 days. From the resulting solution, which on cooling formed a semi-opaque, gelatinous mass, unaltered ethyl iodide was removed by distillation; the alcoholic liquid was then poured into much ether, and the product washed with water and evaporated to dryness. The amorphous, horn-like mass was dissolved in boiling alcohol, allowed to partially cool, and a small quantity of an indefinitely crystalline substance (c) which separated, was rapidly removed by filtration through calico. This operation had for its object the removal of a less soluble ether if such should be present, as is the case with the methylation product. The filtrate became gelatinous on cooling, and as other solvents did not yield a crystalline product, it was evaporated to dryness and acetylated in the hope that the resulting compound would be easier to manipulate. This was found to be the case, for the *monoacetyl* derivative,  $C_{14}H_7O_8(O \cdot C_2H_5)_2 \cdot C_2H_5O$ , crystallised in colourless needles melting at  $168-170^\circ$ .

0.1120 gave 0.2780  $CO_2$  and 0.0575  $H_2O$ .  $C = 67.68$ ;  $H = 5.70$ .

0.4165 „ 0.3670  $C_{18}H_{18}O_5$ .  $C_{18}H_{18}O_5 = 88.11$ .

$C_{20}H_{20}O_6$  requires  $C = 67.41$ ;  $H = 5.62$ ;  $C_{18}H_{18}O_5 = 88.20$  per cent.

The *genistein diethyl ether* regenerated from the above substance could now be crystallised from alcohol, in which it is sparingly soluble, and was thus obtained in colourless needles melting at  $132-134^\circ$ . The mother liquor should be removed while still warm, as the later separations are deposited in the gelatinous condition.

0.1087 gave 0.2752  $CO_2$  and 0.0573  $H_2O$ .  $C = 69.04$ ;  $H = 5.85$ .

0.0645 „ 0.1005  $AgI$ .  $C_2H_5 = 19.22$ .

$C_{18}H_{18}O_5$  requires  $C = 68.79$ ;  $H = 5.73$ ;  $C_2H_5 = 18.47$  per cent.

The ether was decomposed with alcoholic potash and the products separated in the same manner as those yielded by the dimethyl ether. The acid thus obtained formed colourless leaflets melted at  $88^\circ$ , and had the properties of *p*-ethoxyphenylacetic acid,  $C_2H_5 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ .

0.1051 gave 0.2546  $CO_2$  and 0.0593  $H_2O$ .  $C = 66.06$ ;  $H = 6.27$ .

$C_{10}H_{12}O_3$  requires  $C = 66.66$ ;  $H = 6.66$  per cent.

The accompanying phenol is most probably phloroglucinol mono-ethyl ether, but owing to lack of data this cannot yet be identified. When treated with disazobenzene sulphate in the usual manner, an orange-red compound resulted, which crystallised from alcohol in needles, and was insoluble in cold aqueous alkalis.

The product (c) obtained during the purification of the above substance melted at 127—129°, and did not appear to contain a second ethyl ether, although, as a mere trace was available, it could not be properly examined.

Experiments were carried out in the hope of preparing a pure azo-benzene derivative of genistein, but these, as well as those for the production of nitro-derivatives, were unsuccessful; they indicated, however, that if sufficient material were available for the determination of the necessary conditions, such derivatives could be produced, as has been the case with the somewhat closely allied colouring matter apigenin.

#### *Summary of Results.*

When methylated, genistein, like luteolin (*loc. cit.*), gives two ethers which are insoluble in aqueous alkalis, and capable of forming monoacetyl derivatives. That melting at 137—139° is the normal dimethoxy-compound, whereas the second, which melts at 200—202°, is considered to be methylgenistein dimethyl ether. It is probable that the formation of the latter is due to a methyl group entering the ring of the phloroglucinol nucleus during methylation, for there is no evidence to show that methylgenistein (or its glucoside) is contained in *Genista tinctoria*. The production of *p*-methoxy- and *p*-ethoxy-phenylacetic acids from the corresponding ethers of genistein proves that the acid previously obtained from this colouring matter is *p*-hydroxyphenylacetic acid; and the results, as a whole, are in harmony with the constitution which was previously assigned to genistein.

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### CXXVI.—*Luteolin. Part III.*

By ARTHUR GEORGE PERKIN, F.R.S.E., and LOUIS HUBERT HORSFALL.

In previous communications (Trans., 1896, 69, 206, 799), it was shown that luteolin has properties which harmonise with those of a tetra-hydroxy-flavone. The present work was undertaken to support this view and to throw light on some obscure points which occur in these investigations.

It has been shown (*loc. cit.*) that the isolation of luteolin from weld, at best a laborious task, is much simplified by the method devised by one of us, and this process has been again employed. An improvement is effected by adding a concentrated alcoholic solution of the very crude luteolin to ether, omitting the preliminary extraction with this solvent. After removing insoluble matter, the ethereal liquid is washed with water, evaporated to dryness, and the yellow residue submitted to purification. If for this purpose crystallisation from dilute alcohol is employed; and the mother liquors are worked up as far as possible, a small quantity of a product eventually remains which does not crystallise readily, and tends to gelatinise. As the bulk of this residue, unlike luteolin, gave no insoluble hydrobromide in the presence of acetic acid, this method could be employed for its isolation. The acetic acid filtrate from the luteolin hydrobromide was poured into water, the dull yellow precipitate collected, well washed with water, and dried. A solution of this product containing a trace of acetic acid was now treated with lead acetate solution so long as a precipitate formed, and this was filtered off and thoroughly washed with boiling alcohol. The filtrate, after evaporation to a small bulk, was treated with a little boiling water, the semi-crystalline deposit collected, and further purified by crystallisation from alcohol. Examination of the product by Zeisel's method proved the absence of a methoxy-group, but it was observed that by the action of the hydriodic acid a purer substance was obtained. The main bulk was therefore treated in this manner, and finally crystallised from dilute alcohol.

0.1082 gave 0.2617  $\text{CO}_2$  and 0.0389  $\text{H}_2\text{O}$ . C = 65.96; H = 3.99.

0.1156 „ 0.2792  $\text{CO}_2$  „ 0.0413  $\text{H}_2\text{O}$ . C = 65.87; H = 3.96.

$\text{C}_{15}\text{H}_{10}\text{O}_6$  requires C = 66.66; H = 3.70 per cent.

The substance formed almost colourless leaflets, and when heated showed signs of melting at  $235^\circ$ , being completely liquid at  $344^\circ$ . With alcoholic lead acetate solution, it is partially precipitated as a yellow lead compound, and with alcoholic ferric chloride a brown coloration was produced. It was readily distinguished from luteolin by its feeble dyeing properties.

On fusion with caustic potash at  $210^\circ$ , the substance yielded *phloroglucinol* (m. p.  $210^\circ$ ), *p-hydroxybenzoic acid* (m. p.  $209-210^\circ$ ), and traces of *protocatechuic acid* and a substance resembling *p-hydroxyacetophenone*. These results indicated that it was apigenin, which exists as a glucoside in parsley, and as the glucoside of its methyl ether\* in the leaves of

\* This apigenin methyl ether, acacetin, seems to be identical with that recently prepared by Vongerichten, which contains the methoxy-group in the 4'-position (*Ber.*, 1900, 33, 2908); its examination will be continued.

*Robinia pseudacacia* (Trans., 1900, 77, 430). It has been shown by Vongerichten (*Ber.*, 1900, 33, 2334) that the presence of proto-catechuic acid in the decomposition products of apigenin previously observed by himself (*Ber.*, 1876, 9, 1124), and later by one of us (Trans., 1897, 71, 805), is due to a contamination of the apigenin from parsley with luteolin monomethyl ether, and the reappearance of this acid here, as well as the slightly low analytical numbers given above, were evidence that our substance still contained a trace of luteolin. The remaining portion was therefore dissolved in alcohol, the solution treated with a little lead acetate, and the colouring matter recovered from the filtrate in the manner previously given. It now melted at 342—344°, a temperature which nearly coincides with the melting point of synthetical apigenin (347°) given by Czajkowski, von Kostanecki, and Tambor (*Ber.*, 1900, 33, 1992). To remove all doubt on the point, the substance (0.75 gram) was converted into its methyl ether, which crystallised in pale yellow needles melting at 166—167°, and was evidently identical with the apigenin dimethyl ether previously described. The percentage of apigenin in weld appears to be very small, as the quantity of pure substance isolated for these experiments was only 1.5 grams from 31 lbs. of weld extract. Owing, however, to the fact that apigenin is partially precipitated by alcoholic lead acetate, it is obvious that the above does not represent the full amount present in the extract.

#### *Methylation of Luteolin.*

It has been shown (*loc. cit.*) that when methylated, luteolin yields an almost colourless substance melting at 191—192°, which contains three methoxy-groups; to this the formula  $C_{15}H_9O_6(CH_3)_4$  was assigned. Subsequently, Herzig (*Monatsh.*, 1896, 17, 421) expressed the view that this substance was probably the trimethyl ether,  $C_{15}H_7O_6(O\cdot CH_3)_3$ , and not a tetramethyl compound. As analytical numbers a trifle lower than those given at first were afterwards obtained, this view of its composition was adopted. The explanation previously suggested by one of us that a methyl group had entered the ring appeared also unlikely, judging from the behaviour of analogous colouring matters of the quercetin type; moreover, the small yield amounting approximately to 7 per cent. from the exceedingly expensive luteolin, rendered its examination extremely difficult. After careful consideration and a further experience of this class of substance, however, it was difficult to believe that this was the normal trimethyl ether,  $C_{15}H_7O_6(O\cdot CH_3)_3$ , as its melting point was not only particularly high, but its crystalline property did not resemble that of the corresponding triethyl ether. Later (Trans., 1899, 75, 835), it was noted that genistein

when methylated forms two dimethoxy-compounds, one having, like the luteolin compound, a high melting point, whereas the second appeared to be the normal compound. The difficulties involved in the preparation of large quantities of genistein rendered the full examination of its ether of high melting point practically impossible, but it appeared likely that its constitution could be settled by the investigation of the seemingly analogous luteolin derivative.

For this investigation 30 grams of luteolin were methylated in the manner already described\* and 2.5 grams of the pure compound were obtained melting at 191—192°. With alcoholic potash, a potassium salt crystallising in fine yellow needles resulted, which was decomposed by water with regeneration of luteolin.

Previous analyses (*loc. cit.*) gave C=66.86; 66.92; H=5.71, 5.58 per cent.

0.1278 gave 0.2596 AgI.  $\text{CH}_3=12.97$ .

$\text{C}_{16}\text{H}_9\text{O}_8(\text{O}\cdot\text{CH}_3)_8$  requires C=66.66; H=5.26;  $\text{CH}_3=13.17$  per cent.

The acetyl derivative was again prepared and melted at 175—176°, a degree higher than previously stated. Analysis showed that it contained but one acetyl group.

0.5261 gave 0.4666  $\text{C}_{19}\text{H}_{18}\text{O}_6$ . Found 88.69.

$\text{C}_{19}\text{H}_{17}\text{O}_6\cdot\text{C}_2\text{H}_5\text{O}$  requires  $\text{C}_{19}\text{H}_{18}\text{O}_6=89.06$  per cent.

So far, therefore, the results accorded with those required by a luteolin trimethyl ether.

It was now decomposed with alcoholic potash at 160°, and the products separated as described in connection with the triethyl ether (*loc. cit.*). An acid identified as *veratric acid* (m. p. 176—178°) was thus obtained, together with a syrupy phenolic product, which on standing crystallised in slender needles. As the small quantity of the latter rendered its identification as such doubtful, its azobenzene derivative was examined, for in this manner it has been possible to identify the phenolic decomposition products of rhamnazin and other ethers of this class (Perkin and Allison, *Proc.*, 1900, 16, 181).

Diazobenzene sulphate was added to a solution of the phenol in aqueous sodium carbonate, and the orange-red precipitate collected, washed, dried, and purified by crystallisation from alcohol.

0.0574 gave 7.9 c.c. nitrogen at 20° and 748 mm. N=15.49.

$\text{C}_8\text{H}_8\text{O}_8(\text{N}_2\cdot\text{C}_6\text{H}_5)_2$  requires N=15.47 per cent.

The disazo-compound was obtained as a spongy mass of orange-red needles melting at 198—201° and insoluble in cold aqueous alkalis.

\* The yield was not increased by redigesting the product of the reaction with further quantities of methyl alcoholic potash and methyl iodide.

From the results given below, it is evident that this compound is a phloroglucinol derivative; it is not, however, disazobenzenephloroglucinol monomethyl ether (*loc. cit.*), or disazobenzenephloroglucinol itself (Trans., 1897, 73, 816), for these substances melt respectively at 251—252° and 228—230°. From the temperature employed in the decomposition of the trimethyl ether, it is evident that the phenol from which it was derived contains a methoxy-group, and there is thus a strong probability that this compound is *disazobenzenemethylphloroglucinol monomethyl ether*. Consequently, it is assumed that the methyl ether melting at 191—192° contains a methyl group in the phloroglucinol nucleus, and is a *methyl-luteolin trimethyl ether*.

It was interesting, therefore, to examine the colouring matter produced by the decomposition of this ether by means of hydriodic acid. The operation was carried out in the usual manner, the product crystallised from dilute alcohol, and extracted with boiling benzene to remove unaltered ether if present.

0.1011 gave 0.2373 CO<sub>2</sub> and 0.0428 H<sub>2</sub>O. C = 64.00; H = 4.70.

C<sub>16</sub>H<sub>12</sub>O<sub>6</sub> requires C = 64.00; H = 4.00 per cent.

The compound was obtained as glistening leaflets, identical in appearance and general reactions with luteolin itself. Fused with alkali, it yielded a substance having the *phloroglucinol* reaction, but as a mere trace of the colouring matter was available for the experiment, this phenol could not be isolated in a pure condition. It has been shown that the trimethyl ether gives veratric acid; thus the acid product of the above decomposition is *protocatechuic acid*.

The *acetyl* compound of this colouring matter formed colourless needles, sparingly soluble in alcohol, and melted at 239—240° when rapidly heated, and at 235—236° when the operation was conducted slowly. This is considerably higher than the melting point of acetyl-luteolin found by us (222—225°) or by Herzig (221—225°), and again distinguishes it from luteolin.

The melting point of methyl-luteolin is apparently lower than that of luteolin (327—329°), and is provisionally given at 307—309°. As the trace available did not admit of recrystallisation, we leave the point undecided until a larger specimen is available, although this value is probably correct.

*More soluble Product of the Reaction.*—It has been previously stated (Trans., 1897, 73, 191) that in addition to the above compound some quantity of a second is produced by the methylation of luteolin in the manner described. From the mother liquors emanating from the purification of the ether of high melting point, this separated on complete concentration. More was obtained on concentration.

Primary crystallisations from alcohol, with the aid of



animal charcoal to remove a brown impurity, the product was fractionally crystallised from benzene. A first deposit consisted of almost colourless, warty nodules of the ether of high melting point, but the main bulk separated in long needles containing benzene of crystallisation, and these were collected apart, recrystallised from benzene, then repeatedly from mixtures of alcohol and other solvents, and finally from alcohol alone. Thus obtained, the product melted at 157—158°, and was apparently pure; subsequently it was observed that by the decomposition of its acetyl compound, the regenerated substance melted at 161—163°. The difficulty of obtaining the compound in this condition of purity was remarkable when compared with the comparative facility with which the analogous ethers of genistein are separated. Possibly a trace of the methyl luteolin trimethyl ether of high melting point contaminated the product, although this seems to be unlikely judging from the methods adopted.

0.1202 gave 0.2897  $\text{CO}_2$  and 0.0565  $\text{H}_2\text{O}$ .  $\text{C} = 65.73$ ;  $\text{H} = 5.22$ .

0.1940 „ 0.4180  $\text{AgI}$ .  $\text{CH}_3 = 13.75$ .

$\text{C}_{15}\text{H}_7\text{O}_8$  ( $\text{O}\cdot\text{CH}_3$ )<sub>3</sub> requires  $\text{C} = 65.85$ ;  $\text{H} = 4.88$ ;  $\text{CH}_3 = 13.72$  per cent.

This ether was obtained as glistening, lemon-yellow needles, somewhat sparingly soluble in alcohol. With alcoholic potash, it gives a bright yellow salt in the form of minute needles, soluble in 50 per cent. alcohol to form a pale yellow liquid, and is thus more stable in the presence of water than the methyl luteolin compound. This was also evident from the fact that although luteolin trimethyl ether is insoluble in aqueous alkali, it dissolves appreciably in a 50 per cent. alcoholic solution of potassium hydroxide. The *monoacetyl* compound, referred to above, formed colourless prisms readily soluble in alcohol and melted at 156—158°.

0.4536 gave 0.4038  $\text{C}_{18}\text{H}_{16}\text{O}_8$ . Found 89.02 per cent.

$\text{C}_{15}\text{H}_6\text{O}_8(\text{O}\cdot\text{CH}_3)_3\cdot\text{C}_2\text{H}_5\text{O}$  requires  $\text{C}_{18}\text{H}_{16}\text{O}_8 = 88.65$  per cent.

On decomposition with alcoholic potash, the trimethyl ether gave *veratric acid*, and a syrupy phloroglucinol derivative which did not crystallise on long standing. From the latter, an azobenzene derivative was obtained crystallising in orange-red needles melting at 251—252°, identical with *disazobenzene phloroglucinol monomethyl ether* prepared previously from quercetin tetramethyl ether. These decomposition products prove that this compound is the *normal luteolin trimethyl ether*, and with this its crystalline appearance and melting point are in harmony.

The luteolin formed by the decomposition of this ether by means of hydriodic acid was compared with that prepared from weld itself. The latter, purified as above stated by means of its hydrobromide to

remove apigenin, was now converted into the sulphate and this decomposed, as an extra precaution. The product crystallised in needles; it melted at 327—329°, and its acetyl compound at 222—225°. Luteolin, prepared by a 3 hours digestion of the trimethyl ether, crystallised from dilute alcohol in glistening leaflets melting at 314—316°; this was again treated with hydriodic acid for 2 hours, and was then obtained as needles. Its acetyl compound melted at 222—225°, and the colouring matter regenerated from this at 323—326°. The final product separated as a mixture of needles and leaflets, and luteolin thus seems to crystallise in two forms. Luteolin from weld, after the removal of apigenin, is therefore most probably a single substance, for these results show its practical identity with the luteolin prepared from the trimethyl ether. Vongerichten (*Ber.*, 1900, 33, 2334) has given the melting point of luteolin prepared from its monomethyl ether as 326—328°, and in other papers, including that by one of us, it has been stated to lie above 320°. As it appeared evident that weld does not contain methyl-luteolin, the formation of this compound as its trimethyl ether could only be due to the entrance of a methyl into the ring during methylation. An attempt to prepare this compound by digesting luteolin trimethyl ether (1 gram) dissolved in a solution of potassium hydroxide (1 gram) in methyl alcohol with excess of methyl iodide for 2 days was unsuccessful, no change of this nature having occurred. Possibly the entrance of the methyl into the ring occurs simultaneously with the methylation of a hydroxyl group probably adjacent, and cannot be effected later, at least in the above manner. It is interesting to note that the methyl-luteolin compound can be obtained from luteolin prepared from the *Genista tinctoria* (*loc. cit.*), and is also described by Vongerichten as obtainable from the luteolin monomethyl ether contained in parsley (*loc. cit.*).

#### *Luteolin Dimethyl Ether.*

It was suggested by one of us that scoparin\* (*Trans.*, 1900, 77, 423) is a derivative of a luteolin monomethyl ether, possibly its stable glucoside. In the hope of preparing this ether, which should have the methoxy-group in the 3' position, the partial methylation of luteolin was studied.

\* In the preliminary notice on scoparin (*Proc.*, 1899, 15, 123), the investigations of Goldschmidt and Hemmelmayr (*Monatsh.*, 1898, 14, 202; 1894, 15, 316) have been overlooked. The recognition of the presence of a methoxy-group in scoparin, and its decomposition into phloroglucinol and acetovanillone, considered to be new at the time, thus merely corroborate their work; although this will be more fully explained in an investigation of scoparin which I hope shortly to communicate, I take this opportunity of expressing regret to these chemists that the oversight has occurred.—A. G. P.

Five grams of luteolin dissolved in a solution of 3 grams of potassium hydroxide in methyl alcohol were treated with 12 grams of methyl iodide and digested at the boiling point for 2 days. A deposit separated on cooling, and this was collected, washed with water containing a little sulphurous acid, then with alcohol, and repeatedly recrystallised from the latter solvent until its melting point was constant.

0.1065 gave 0.1656 AgI.  $\text{CH}_3 = 9.92$ .

$\text{C}_{15}\text{H}_8\text{O}_4(\text{O}\cdot\text{CH}_3)_2$  requires  $\text{CH}_3 = 9.55$  per cent.

This ether formed a glistening mass of almost colourless needles, soluble in aqueous alkalis with a pale yellow coloration, and melted at  $224-225^\circ$ . The yield was small, amounting only to about 8 per cent of the luteolin employed, and but little loss was experienced during its isolation owing to its sparing solubility in alcohol. It did not dye mordanted calico. To determine the position of the methoxy-groups in this substance, it was decomposed with alcoholic potash at  $160^\circ$ . From the products of the reaction, an acid was isolated in the form of colourless needles melting at  $250^\circ$ , identical with *isovanillic acid*. The phenol simultaneously produced was not examined, as the fact that methylation can be effected by the method just described indicated that the hydroxyl group occupies the para- and not the ortho-position relatively to the carbonyl group. It is interesting to note that Vongerichten's methyl ether of luteolin from parsley (*loc. cit.*) has its methoxy-group in the same position (4') as that occupied by one of those in the above compound.

The mother liquors obtained in the purification of the dimethyl ether contained a mixture of substances, from which we are not yet satisfied that a pure product has been isolated. By fractional crystallisation from alcohol, an impure monomethyl ether was separated (found  $\text{C} = 64.16$ ;  $\text{H} = 4.31$ .  $\text{C}_{10}\text{H}_{12}\text{O}_6$  requires  $\text{C} = 64.00$ ;  $\text{H} = 4.00$  per cent.), and this on decomposition gave *isovanillic acid*. As an ether yielding in this way not *isovanillic* but *vanillic acid* was the one desired, the above compound was not closely studied, but further experiment will now be made, as this should prove to be identical with Vongerichten's natural methylluteolin. The residue from the above methyl ethers gave shades, notably as regards the iron mordant, resembling in character although somewhat stronger than those given by scoparin. The subject will be further studied when a larger quantity of luteolin has been prepared.

*Decomposition Product of Luteolin.*

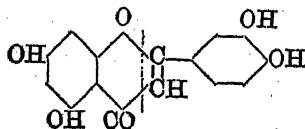
When fused with alkali to 170—200°, luteolin yields protocatechuic acid and phloroglucinol. If the tetrahydroxyflavone constitution assigned to it by one of us be correct, an acetophenone derivative, if it possesses sufficient stability, should be formed at a lower temperature under the conditions of the reaction. In this manner, for instance, chrysin (dihydroxyflavone) and apigenin (trihydroxyflavone) give respectively acetophenone and *p*-hydroxyacetophenone. Three grams of luteolin dissolved in 100 c.c. of a 50 per cent. solution of potassium hydroxide were digested at the boiling point for about half an hour, or until a sample of the solution when neutralised with acid deposited only a trace of unaltered colouring matter. The yellow liquid was now acidified, extracted with ether, the extract evaporated, the residue dissolved in water, treated with excess of sodium hydrogen carbonate, and again extracted with ether. On evaporation, an oily residue remained which crystallised on standing, and this was repeatedly extracted with boiling benzene. From this solution, the bulk of the benzene was removed by distillation, and the crystals which separated from the residual liquid on cooling were collected and recrystallised from benzene with the aid of animal charcoal.

0.0647 gave 0.1506 CO<sub>2</sub> and 0.0327 H<sub>2</sub>O. C = 63.47; H = 5.61.

0.1103 „ 0.2555 CO<sub>2</sub> „ 0.0545 H<sub>2</sub>O. C = 63.17; H = 5.49.

C<sub>8</sub>H<sub>8</sub>O<sub>3</sub> requires C = 63.16; H = 5.26 per cent.

The product was deposited from benzene in needles containing benzene of crystallisation; this evaporated at the ordinary temperature and the compound then melted at 114—116°. With aqueous ferric chloride it gave a deep green liquid, and was decomposed by fused alkali at 200° with formation of protocatechuic acid. It was thus identical with the *acetyl catechol*, C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>·CO·CH<sub>3</sub>, prepared synthetically by Dzierzgowski (*J. Russ. Phys. Chem. Soc.*, 25, 157). The residue insoluble in the benzene proved to be *phloroglucinol*, and these products confirm the tetrahydroxyflavone constitution,



previously assigned to luteolin by one of us.

It is interesting to notice that whereas apigenin (*Trans.*, 1897, 71, 817) has been shown to be hydroxychrysin, the above results indicate that luteolin is *hydroxyapigenin*.

*Salts of Luteolin.*

It was found (Trans., 1899, 75, 433) that as a rule phenolic colouring matters containing two hydroxyls in the ortho-position relatively to one another decompose the alkali acetates, forming mono-substituted salts. The products then obtained from luteolin in this manner, being gelatinous, were not fully examined. Experiments now show that if a saturated alcoholic solution of luteolin is treated with potassium acetate, and then, while boiling, with a few drops of water, a crystalline salt separates on cooling. This was collected, washed with water, and dried at 160°.

0.4990 gave 0.1340  $K_2SO_4$ .  $K = 12.03$ .

0.5053 „ 0.1350  $K_2SO_4$ .  $K = 11.97$ .

0.6559 decomposed with acid gave 0.5800  $C_{15}H_{10}O_6$ .  $C_{15}H_{10}O_6 = 88.42$ .

$C_{15}H_9O_6K$  requires  $K = 12.03$ ;  $C_{15}H_{10}O_6 = 88.27$  per cent.

*Monopotassium luteolin* forms fine yellow needles, and is decomposed by boiling water with separation of luteolin. It closely resembles the corresponding quercetin salt.

The *sodium* compound is obtained by employing a dilute alcoholic solution of sodium acetate in place of the potassium salt. If crystals do not separate on cooling, water is added drop by drop, and the mixture boiled after each addition. The product is washed first with alcohol, then with water, and finally with alcohol.

Analyses were made with distinct preparations.

0.3696 gave 0.0424  $Na_2SO_4$ .  $Na = 3.71$ .

0.4968 „ 0.0584  $Na_2SO_4$ .  $Na = 3.80$ .

$C_{20}H_{19}O_{12}Na$  requires  $Na = 3.87$  per cent.

The sodium salt of luteolin is thus analogous to the potassium salts of rhamnetin and rhamnazin (*loc. cit.*) as it is a mono-sodium derivative of a double molecule of the colouring matter.

*Summary of Results.*

On methylation, luteolin from weld yields, not only the normal trimethyl ether, but a second substance, which is regarded as methyl-luteolin trimethyl ether. This appears to be produced by the entrance of a methyl into the ring of the phloroglucinol nucleus during the methylation process, rather than to result from the presence of methyl-luteolin (as glucoside) in weld itself, and it is pointed out that luteolin from the *Genista tinctoria* (*loc. cit.*) and luteolin monomethyl ether from parsley (Vongerichten, *loc. cit.*), also yield this compound. By the ethylation of luteolin, Herzig (*loc. cit.*) has found that, in

addition to the expected triethyl ether, a tetraethyl ether is formed to some extent, so that, in these respects, this colouring matter behaves analogously to resacetophenone (Gregor, *Monatsh.*, 1894, 15, 437) and  $\beta$ -resorcylic acid (Trans., 1895, 67, 995). Curiously enough also genistein (this vol., p. 1310) forms two similarly constituted dimethyl ethers. Other members of the flavone group do not appear to possess this property, for, as a general rule, the hydroxyl adjacent to the carbonyl group is not etherified in the ordinary manner of working, [although Friedländer (*Ber.*, 1897, 30, 2154) speaks of a chrysin dimethyl ether received from Piccard for purposes of comparison. Although there is little doubt that methyluteolin trimethyl ether has the constitution assigned to it, it is proposed to further investigate this substance in the hope of isolating methylphloroglucinol from among its decomposition products. Much luteolin will be necessary for this purpose, and as this is difficult to prepare, the publication of the results may be delayed for some time. The decomposition of luteolin into acetylcatechol and phloroglucinol practically establishes the tetrahydroxyflavone constitution previously assigned to it (*loc. cit.*). In addition to luteolin, weld contains a trace of apigenin, and to this is no doubt due the slightly lower melting point previously assigned to acetyluteolin.

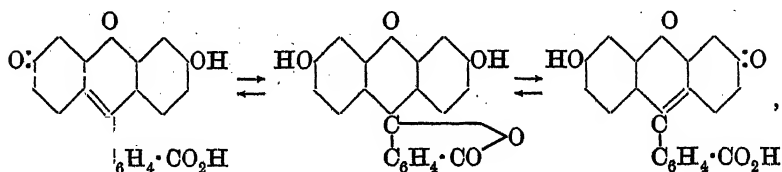
CLOTHWORKERS' RESEARCH LABORATORY,  
DYEING DEPARTMENT,  
YORKSHIRE COLLEGE.

## CXXVII.—Contributions to the Knowledge of Fluorescent Compounds. Part I. The Nitro-derivatives of Fluorescein.

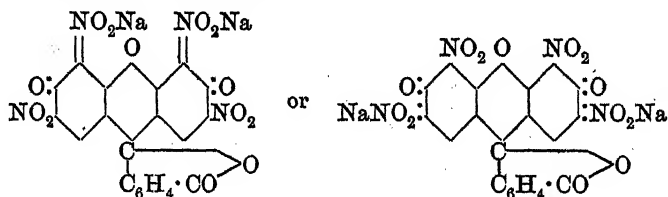
By JOHN THEODORE HEWITT and BRYAN W. PERKINS.

It is a remarkable fact that whereas the tetrabromo- and tetraiodo-derivatives of fluorescein show marked fluorescence in alkaline solutions, the corresponding nitro-compound exhibits no trace of this property. This fact has already been commented on by Richard Meyer (*Zeit. physikal. Chem.*, 1897, 24, 468) and by one of the authors of the present communication (Proc., 1900, 16, 3; *Zeit. physikal. Chem.*, 1900, 34, 1). Meyer, noticing that tetraiodofluorescein fluoresces less than tetrabromofluorescein, and this, in turn, less than fluorescein itself, would have been inclined to attribute the decrease in the fluorescence to an

increase in the mass of the substituent groups, were it not that an alkaline solution of tetranitrofluorescein shows no trace of fluorescence whatever, although  $\text{NO}_2=46$ , whilst  $\text{Br}=80$  and  $\text{I}=127$ . The view put forward by one of the present authors, that in the greater number of cases the fluorescence of organic compounds is caused by a doubly symmetrical tautomerism, furnishes a satisfactory explanation of the fluorescence of fluorescein, eosin, and tetraiodofluorescein where the only tautomerism possible is indicated in the following scheme :



whereas, for a nitro-derivative in which a nitro-group stands in the ortho-position relatively to a hydroxyl-group, it is not only possible, but indeed probable, that the nitrophenol group itself reacts tautometrically, producing a salt in which the metal is attached to the nitroxyl, and not to the hydroxyl grouping. The sodium salt of tetranitrofluorescein should then possess one of following constitutions :



In this case, the configuration would be stable enough to preclude tautomerism, due to the opening of the lactone ring, the oxygen of the hydroxyl groups having been previously transformed into the quinonoid form and sodium ions, thus losing their chance of migrating to the carboxyl group of the lactone ring.

If this view were correct, an exactly similar argument should apply to dinitrofluorescein, but although the so-called hydrate of dinitrofluorescein, which gives blue, non-fluorescent, alkaline solutions, has been prepared and analysed by von Baeyer (*Annalen*, 1876, 183, 32), the anhydrous substance of the formula  $\text{C}_{20}\text{H}_{10}(\text{NO}_2)_2\text{O}_6$  does not appear to have been analysed. In purifying dinitrofluorescein, von Baeyer acetylated the crude product, recrystallised the diacetyl derivative from alcohol or ethyl acetate, and hydrolysed this by boiling with a solution of potassium or sodium hydroxide. On precipitation of the

resulting blue solution with an acid, a yellow substance was obtained, which, even after recrystallisation, again dissolved in alkalis with a blue colour, von Baeyer's numbers for the compound agreeing with those required for the formula  $C_{20}H_{12}(NO_2)_2O_6$ . These results we can confirm, but by carrying out the hydrolysis of the diacetyl derivative with sulphuric acid instead of with an alkali, we have succeeded in obtaining the anhydrous dinitrofluorescein; we have also introduced various modifications in methods of purification which considerably simplify the process.

Although the anhydrous dinitro-derivative of fluorescein has been obtained and dissolves in cold alkali with the production of an orange-brown solution which evidently contains a salt of a substance of the formula  $C_{20}H_{10}(NO_2)_2O_5$ , the nitro-groups act in the way which might be expected from the generally accepted views as to the constitution of salts of nitrophenols, and preclude the double tautomerism required for fluorescence which would otherwise result from the opening of the lactone ring. The fact that a solution, even if unstable, of a sodium salt of dinitrofluorescein has been obtained, is of considerable importance, since we have thus been able to examine a derivative of fluorescein which, although still possessing the pyrone ring intact, nevertheless shows no fluorescence in alkaline solutions. The real significance of this result will be observed when it is stated that not only are the usual salts of dinitrofluorescein derived from a hydrate, but that in the case of tetranitrofluorescein it has not been possible to isolate any substance other than a hydrate having the formula  $C_{20}H_{10}(NO_2)_4O_6$ . Any arguments which might be drawn from the non-fluorescence of the salts of the so-called tetranitrofluorescein are hence invalid.

*Preparation of Dinitrofluorescein Hydrate.*—In the nitration of fluorescein, von Baeyer's directions with regard to temperature need careful attention. By following his instructions in adding 10 grams of fuming nitric acid to 5 grams of fluorescein dissolved in 100 grams of concentrated sulphuric acid cooled to  $0^\circ$ , and pouring into water immediately after the last addition of nitric acid has been effected, a bright yellow precipitate separates containing very little unaltered fluorescein, much of the dinitro-compound, and always some of the tetranitro-derivative. On the other hand, if the solution is allowed to stand overnight, tetranitrofluorescein is practically the only product, as it also is if the temperature is allowed to rise unduly. A very convenient method of separating the tetranitro- and dinitro-derivatives from one another is either to digest the mixture with a solution of sodium acetate, or to dissolve the whole precipitate obtained by pouring into water in hot, dilute sodium hydroxide, and then to precipitate the dinitro-compound with acetic acid, the solution being allowed to cool



before filtering, as the dinitrofluorescein hydrate is fairly soluble in hot water. The colour exhibited by an alkaline solution of the residue shows that it is an almost pure dinitro-compound; for most purposes, it is merely necessary to recrystallise the substance from hot alcohol, whereby small, orange, rhomboidal plates are obtained, which dissolve in cold alkali with a beautiful blue colour. The solution, however, occasionally shows a slight green fluorescence, due to the presence of unattacked fluorescein. If this is the case, it is best to acetylate the product with acetic anhydride, and to recrystallise the acetyl derivative from glacial acetic acid until a sample gives an alkaline solution from which all fluorescence is absent. We confirmed the composition of the dinitrofluorescein hydrate so obtained by analysis:

0.1393 gave 0.2799  $\text{CO}_2$  and 0.0335  $\text{H}_2\text{O}$ .  $\text{C} = 54.80$ ;  $\text{H} = 2.67$ .

0.2155 „ 12.1 c.c. moist nitrogen at  $15^\circ$  and 768 mm.  $\text{N} = 6.65$ .

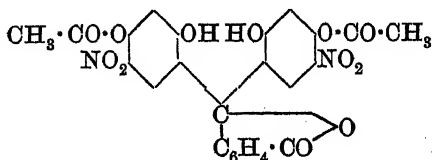
$\text{C}_{20}\text{H}_{12}\text{O}_{10}\text{N}_2$  requires  $\text{C} = 54.52$ ;  $\text{H} = 2.75$ ;  $\text{N} = 6.38$  per cent.

*Diacetyldinitrofluorescein*.—On acetylating dinitrofluorescein hydrate, water is split off, and the diacetyl derivative of dinitrofluorescein produced. This acetyl derivative also results on the acetylation of the crude product formed by adding nitric acid to the sulphuric acid solution of dinitrofluorescein, as von Baeyer has previously shown, whilst naturally it may also be obtained, in better yield and of greater purity, by the action of acetic anhydride on the residue left after the crude nitration product is extracted with a dilute sodium acetate solution. It crystallises in colourless rosettes of needles from glacial acetic acid. On analysis:

0.1729 gave 0.3632  $\text{CO}_2$  and 0.0450  $\text{H}_2\text{O}$ .  $\text{C} = 57.28$ ;  $\text{H} = 2.87$ .

$\text{C}_{24}\text{H}_{14}\text{O}_{11}\text{N}_2$  requires  $\text{C} = 56.91$ ;  $\text{H} = 2.76$  per cent.

When diacetyldinitrofluorescein is boiled continuously for 10 hours with a mixture of ethyl alcohol and water to which ethyl acetate is added to increase its solubility, a yellow solution is obtained from which, on evaporation of the ethyl acetate and cooling of the mother liquors, small, yellow crystals separate out which partially dissolve in hot sodium carbonate or cold sodium hydroxide (a residue of unattacked diacetyl derivative being left) with an orange colour. On boiling with caustic soda, a blue colour is produced, as might be expected. The substance might be dinitrofluorescein from the colour of its solutions, although this is impossible, since the continued boiling with ethyl alcohol and water would convert any such compound into the hydrate, which dissolves with a blue shade in cold sodium hydroxide. Since the diacetyldinitrofluorescein is insoluble in soda, there seems only one possibility left, namely, that water has been added on to the substance, and a hydrate of the constitution



produced. The orange colour of the alkaline solution is precisely what might be expected from a nitrophenolic compound of this type.

*Tetrasodium Salt of Dinitrofluorescein Hydrate.*—When a solution of an excess of sodium ethoxide in absolute alcohol is added to a hot saturated alcoholic solution of dinitrofluorescein, an orange colour is observed changing to blue on the addition of a few drops of water. On stirring the solution, a crystalline, purple paste rapidly separates. This, when collected and washed with alcohol, was found to contain 4 atoms of sodium per molecule.

0.1993 (dried at 115°) gave 0.1051  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 17.04$ .

0.2217 (dried at 105°) „ 0.0923  $\text{NaCl}$ .  $\text{Na} = 17.30$ .

$\text{C}_{20}\text{H}_8\text{O}_{10}\text{N}_2\text{Na}_4$  requires  $\text{Na} = 17.42$  per cent.

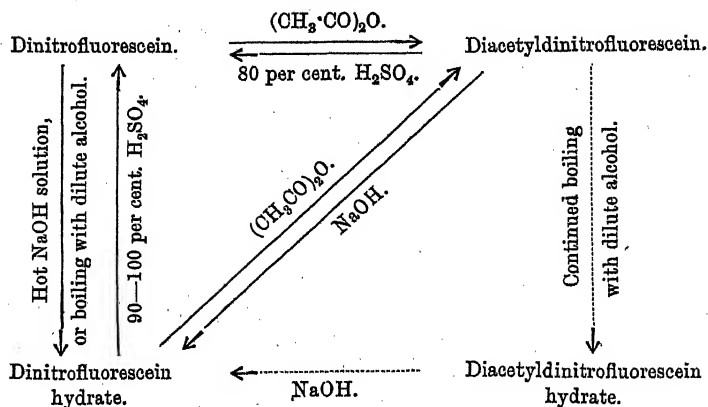
*Anhydrous Dinitrofluorescein*,  $\text{C}_{20}\text{H}_{10}(\text{NO}_2)_2\text{O}_5$ .—This substance may be obtained by heating the diacetyl derivative with five times its weight of 80 per cent. sulphuric acid for an hour on the water-bath. At first a clear brown solution was obtained, from which on further heating a canary precipitate separated, the remainder of the substance being thrown out by water. The dinitrofluorescein thus obtained was ground up to a fine paste with water, well washed, and finally dried at 110°.

0.1347 gave 0.2832  $\text{CO}_2$  and 0.0325  $\text{H}_2\text{O}$ .  $\text{C} = 57.33$ ;  $\text{H} = 2.68$ .

$\text{C}_{20}\text{H}_{10}\text{O}_9\text{N}_2$  requires  $\text{C} = 56.80$ ;  $\text{H} = 2.39$  per cent.

The substance is sparingly soluble in strong alcohol, in which it dissolves with a reddish-yellow colour showing no fluorescence; the colour becomes somewhat green in shade on addition of a drop of hydrochloric acid. On long continued boiling with methylated spirit, it dissolves with a red colour and shows no fluorescence, addition of water precipitating the hydrate. It is somewhat soluble in acetic acid, and fairly so in ethyl acetate, from which it separates in small, radiate aggregates of prisms. It dissolves in cold, dilute sodium hydroxide or in sodium carbonate solution with an orange-brown colour; the solution exhibits no fluorescence. On warming a caustic soda solution, the colour soon changes to a deep blue, a salt of the hydrate being produced, but the orange or red solution in sodium carbonate does not become blue on boiling.

The transformations experienced by dinitrofluorescein and its derivatives may be expressed by the following table:



In this scheme, the dotted lines represent changes which have not been confirmed by analyses of the products, diacetyldinitrofluorescein hydrate not having been isolated in a sufficiently pure condition for the purpose.

*Dibenzoyldinitrofluorescein*,  $\text{C}_{20}\text{H}_8(\text{NO}_2)_2(\text{CO}\cdot\text{C}_6\text{H}_5)_2\text{O}_5$ .—This substance was prepared by boiling 3 grams of dinitrofluorescein with 10 grams of benzoyl chloride in a reflux apparatus until the evolution of hydrogen chloride ceased. The product was then poured into alcohol, and stirred until the pasty substance first precipitated became a brown, crystalline powder. This was collected, washed with alcohol, dried, and dissolved in boiling ethyl acetate. The solution was decolorised as far as possible with animal charcoal, filtered, and absolute alcohol added until the liquid began to show turbidity. On standing overnight, a glistening, colourless, crystalline powder had separated, which, under the microscope, proved to consist of rhomboidal plates, the smaller angles of which were about  $75^\circ$ .

0.1626 gave 6.5 c.c. moist nitrogen at  $18^\circ$  and 767 mm.  $\text{N}=4.63$ .

$\text{C}_{24}\text{H}_{18}\text{O}_{10}\text{N}_2$  requires  $\text{N}=4.57$  per cent.

The substance dissolves fairly easily in acetone, ethyl acetate, or pyridine; it is only taken up sparingly by benzene and ethyl alcohol. Its behaviour towards caustic soda solution corresponds with that of the diacetyl derivative.

*Tetranitrofluorescein*.—In preparing this compound von Baeyer acted on fluorescein with a considerable excess of fuming nitric acid (*Annalen*, 1876, 183, 33). We have found that by using corresponding quantities for dinitrofluorescein, but allowing the temperature to rise, or, preferably, the mixture to stand overnight, a very good yield of the tetranitro-derivative is obtained. This is isolated by pouring into water, when a pinkish paste separates, this is filtered, washed, and dis-

solved in a hot solution of sodium acetate. The solution is of a beautiful red colour, and, on cooling, deposits crystals of a sodium salt which, on recrystallisation, separates in small, brilliant red tetrahedra strongly resembling potassium dichromate in appearance. On precipitating the hot solution of the above sodium salt with a mineral acid, a pinkish-white precipitate is obtained, which, after drying, has the composition of a hydrate of tetranitrofluorescein.

0.1650 gave 0.2738  $\text{CO}_2$  and 0.0336  $\text{H}_2\text{O}$ .  $\text{C} = 45.26$ ;  $\text{H} = 2.25$ .

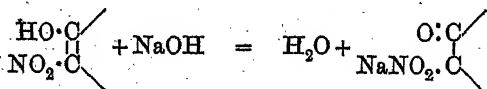
0.1930 „ 18.6 c.c. moist nitrogen at  $24^\circ$  and 768 mm.  $\text{N} = 10.81$ .

0.1948 „ 18.0 c.c. „ „ „  $24^\circ$  „ 754 mm.  $\text{N} = 10.49$ .

$\text{C}_{20}\text{H}_{10}\text{O}_{14}\text{N}_4$  requires  $\text{C} = 45.28$ ;  $\text{H} = 1.90$ ;  $\text{N} = 10.57$  per cent.

$\text{C}_{20}\text{H}_8\text{O}_{18}\text{N}_4$  „  $\text{C} = 46.87$ ;  $\text{H} = 1.56$ ;  $\text{N} = 10.93$  „

Von Baeyer does not mention the existence of a hydrate, but certainly our hydrate shows exactly the colour changes in alcoholic solution which he describes, namely, a yellowish-red colour with a yellowish-green fluorescence, the colour becoming reddish-violet on the addition of a drop of concentrated hydrochloric acid. Noteworthy is the fact that in alkaline solution no fluorescence is observed, which agrees well with the hypothesis of the conversion of the nitrophenol group into the quinone-isonitro-group on addition of alkali.



The analytical numbers obtained by von Baeyer agreed with those required for the formula  $\text{C}_{20}\text{H}_8(\text{NO}_2)_4\text{O}_6$ , and not with those for  $\text{C}_{20}\text{H}_{10}(\text{NO}_2)_4\text{O}_6$ ; his product was, however, recrystallised from glacial acetic acid. It seemed very probable, therefore, that the compound  $\text{C}_{20}\text{H}_{10}(\text{NO}_2)_4\text{O}_6$  had become dehydrated by continued boiling with glacial acetic acid, especially since we had found that dinitrofluorescein hydrate, under similar conditions, yields a product soluble in alkali with an orange colour. We repeated the recrystallisation from acetic acid, and on analysing the recrystallised product were astonished to find that we were still dealing with the hydrate; a repetition of the experiment gave the same result, although the tetranitrofluorescein hydrate was boiled with 50 parts of glacial acetic acid for at least 10 hours. The analyses refer to the two different recrystallised preparations.

0.1855 gave 0.3096  $\text{CO}_2$  and 0.0480  $\text{H}_2\text{O}$ .  $\text{C} = 45.52$ ;  $\text{H} = 2.87$ .

0.1378 „ 0.2280  $\text{CO}_2$  „ 0.0306  $\text{H}_2\text{O}$ .  $\text{C} = 45.12$ ;  $\text{H} = 2.47$ .

The sodium salt above mentioned must be looked upon as a derivative compound,  $\text{C}_{20}\text{H}_{10}(\text{NO}_2)_4\text{O}_6$ .

0.4474 air-dried salt lost 0.0870  $\text{H}_2\text{O}$  at  $110^\circ$ .  $\text{H}_2\text{O} = 19.44$ .

$\text{C}_{20}\text{H}_8\text{O}_{14}\text{N}_4\text{Na}_2 \cdot 8\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 20.06$  per cent.

0.3181 anhydrous salt gave 0.0900  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 8.12$ .

$\text{C}_{20}\text{H}_8\text{O}_{14}\text{N}_4\text{Na}_2$  requires  $\text{Na} = 8.04$  per cent.

$\text{C}_{20}\text{H}_8\text{O}_{13}\text{N}_4\text{Na}_2$  „  $\text{Na} = 8.45$  „

A *barium salt* was obtained by boiling tetranitrofluorescein hydrate with barium carbonate and water so long as carbon dioxide was evolved. The filtered solution deposited small, red crystals on cooling; these contained 4 mols. of water of crystallisation.

0.3263 gave 0.0308  $\text{H}_2\text{O}$  and 0.0979  $\text{BaSO}_4$ . \*  $\text{H}_2\text{O} = 9.45$ ;  $\text{Ba} = 17.59$ .

$\text{C}_{20}\text{H}_8\text{O}_{14}\text{N}_4\text{Ba} \cdot 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 9.77$ ;  $\text{Ba} = 18.62$  per cent.

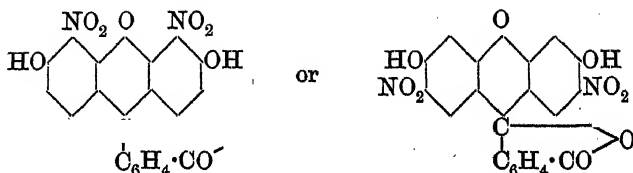
*Acetyl Derivative.*—Von Baeyer mentions the preparation of an acetyl derivative, but gives no analytical data. We have also had such a compound in our hands, but also give no analyses, since every attempt at a combustion ended with an explosion, even when the substance was mixed with copper oxide in a bayonet tube. It is hoped that analytical data will eventually be obtained, as it would be of interest to see if closure of the pyrone ring takes place during acetylation.

*Constitution of the Nitro-derivatives of Fluorescein.*—It will be seen from the experimental details communicated in this paper that the entry of nitro-groups into the fluorescein molecule in the ortho-positions relatively to the hydroxyl groups destroys the fluorescence, dinitrofluorescein giving an orange, non-fluorescent solution with caustic soda, although this solution readily turns blue on standing or heating, the elements of water being added on. This result is of considerable importance, since any arguments deduced from the non-fluorescent character of salts of tetranitrofluorescein are invalidated by the fact that this compound has only been obtained in the form of a hydrate.† Although there is no probability of dinitrofluorescein being other than an *o*-nitrophenol derivative, it nevertheless seemed advisable to determine the orientation of the nitro-groups if this were possible.

Dinitrofluorescein might equally well have either of the two formulæ

\* We were unable to obtain more satisfactory numbers for the percentage of barium, on account of the explosive nature of the salt.

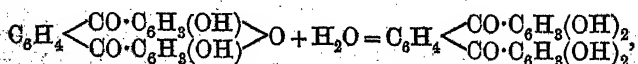
† The term *hydrate* has been used throughout this paper for the derivatives obtained by the addition of water to the fluorescein compounds. These substances, which really result by the opening of the pyrone-ring, are analogues of phenolphthalein and it would be more systematic to give analogous names to them, thus dinitrofluorescein hydrate should be termed dinitroresorcinol-phthalein, &c.



although the latter is, perhaps, slightly more probable, as it avoids so much crowding of substituent groups in the ortho-position. We endeavoured to settle the point by fusion with alkali, a reaction very incompletely studied by von Baeyer (*loc. cit.*, 32). One of the products should be a nitroresorcinol, of which two have been described, the 1:3:4-derivative melting at  $115^\circ$  and the 1:3:2-derivative at  $85^\circ$  (Weselsky, *Annalen*, 1872, 164, 1; *Monatsh.*, 1880, 1, 887; Flitz, *Ber.*, 1875, 8, 631).

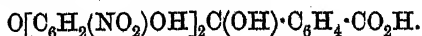
Five grams of dinitrofluorescein hydrate were dissolved in 20 grams of 50 per cent. caustic potash solution and heated in a nickel basin until the blue colour had given place to a yellowish-brown shade. During the fusion, a certain amount of ammonia was evolved. The product was dissolved in water and acidified with hydrochloric acid, upon which a strong smell of hydrocyanic acid was noticeable. The liquid was filtered, the solid residue boiled with water, allowed to cool, and filtered, the operation being repeated several times. Nitroresorcinol, if produced during the fusion, should be found in the aqueous extract, which was in consequence repeatedly shaken with benzene. On distillation of the benzene extract, a small residue was obtained which, after two recrystallisations from water, with the addition of animal charcoal, gave a sufficient quantity of minute yellow crystals for the determination of a melting point. This was found to be  $114^\circ$  (uncorr.).

One point further has to be considered, namely, the position in the molecule where water is added on in the production of the so-called hydrates. In 1876, von Baeyer assumed that, in the production of fluorescein, oxide or ether formation took place between hydroxyl groups of the two resorcinol molecules, which condense with one molecule of phthalic anhydride. On the conversion of a fluorescein compound into a hydrate, this oxygen atom was supposed to take up a molecule of water, the change being represented by the equation

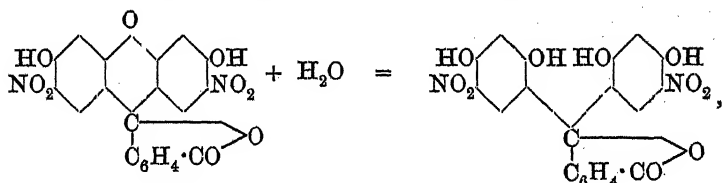


On the substitution of the lactone for the diketonic formula for fluorescein, the idea seems to have arisen that water was added to the

lactone group. For example, in Beilstein's *Handbuch* (2te Aufl. Bd. II., 1296) dinitrofluorescein is formulated as



Such an expression seems to us to be untenable; in its place we would substitute a formula in which the addition of water resulted in the splitting of the pyrone ring in the following manner :



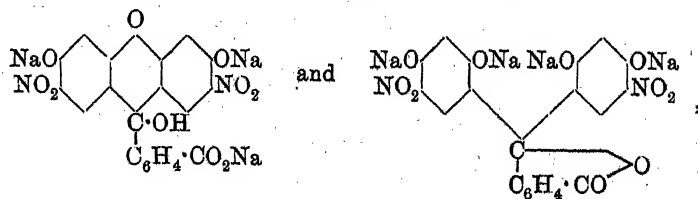
The grounds on which this view is based are as follows.

1. Fluorescein itself is very stable towards alkali, the tetrabromo-derivative takes up water more easily than fluorescein, whilst with dinitrofluorescein the hydrate is the stable form and with tetranitrofluorescein the hydrate is the only form we have so far been able to isolate. Negative groups introduced into a benzene nucleus are known to influence other groups in the same nucleus and especially when the substituents are in ortho- or para-positions relatively to one another. That the negative groups should influence the extranuclear lactone ring, however, is, so far as we are aware, without analogy.

2. The pyrone ring of fluorescein is evidently weakened by the introduction of nitro-groups as shown by the fact that an acridine derivative results when dinitrofluorescein is treated with cold ammonia solution (Reverdin, *Ber.*, 1897, 30, 332).

3. The blue colour of the solution of dinitrofluorescein hydrate in alkali is not dissimilar to the colour exhibited by the phthaleins; at any rate, it resembles this far more than the red or brown solutions produced when fluorescein or fluorone derivatives are dissolved in an alkali. This argument does not lose in weight by the fact that dinitrofluorescein itself dissolves in cold alkali with an orange shade.

4. The formation of a tetra-sodium salt from dinitrofluorescein hydrate affords fairly conclusive evidence in favour of this view; had the lactone ring been opened a trisodium salt would be expected, as is shown on consideration of the two possible formulæ :



As a result of this work the conclusion may be drawn that the introduction of nitro-groups into the fluorescein molecule in the ortho-position relatively to the hydroxyl groups prevents fluorescence in alkaline solutions, owing to the usual phenol-lactone and quinonoid-carboxylic acid tautomerism of fluorescein being inhibited by a secondary tautomerism between the nitro- and phenolic hydroxyl groups. At the same time, the pyrone ring is so much weakened that water is readily added on with production of a true phthalein.

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- 2:3:4-Trimethylbenzoic acid** (*prehnitic acid*) (LAPWORTH and CHAPMAN), T., 311; P., 1900, 4.
- Trimethylbrazilin**, oxidation of, with potassium permanganate (GILBODY, PERKIN, and YATES), P., 1900, 105.
- $\alpha,\beta$ -Trimethylbutyric acid**,  $\gamma$ -cyano-, ethyl ester (THORPE and YOUNG), T., 939; P., 1900, 115.
- Trimethyldihydroresorcylic acid**, ethyl ester and Trimethyldihydroresorcinol and its ethyl ether and bromo-derivatives (CROSSLEY), P., 1900, 90.
- Trimethyldihydroxybenzenes** (COLLIE and STEELE), T., 961; P., 1900, 146.
- trans*-Trimethylenedicarboxylic acid**, formation of (BOWTELL and PERKIN), P., 1899, 242.
- $\alpha,\beta$ -Trimethylglutaric acid** (*hexanedicarboxylic acid*) (CROSSLEY), P., 1900, 91.
- Trimethylhydrindamine iodide**, preparation of, and indene from (KIPPING and HALL), T., 469; P., 1900, 54.
- Trimethylpyrone** (COLLIE and STEELE), T., 961; P., 1900, 146.
- Trimethylsulphine iodide mercuric iodide** (SMILES), T., 161; P., 1899, 240.

Triphenylcarbinol, attempts to prepare ethers of (LANDER), T., 782.

## V.

Valeric acids ( $\alpha$ - and  $\beta$ -methylbutyric acids),  $\gamma$ -cyano-, ethylesters (HOWLES, THORPE, and UDALL), T., 947; P., 1900, 116.

Vanadium, separation of, from sulphuric acid (GOYDER), T., 1096.

Vapour density of dried mercury and of dried mercurous chloride (BAKER), T., 646; P., 1900, 68.

Vapour pressure of camphor (ALLEN), T., 418; P., 1899, 185.

of diisopropyl and diisobutyl (YOUNG and FORTEY), T., 1126; P., 1900, 165.

of naphthalene (ALLEN), T., 400; P., 1899, 122.

of *n*-octane (YOUNG), T., 1145; P., 1900, 166.

Vitexin, constitution of (PERKIN), T., 422; P., 1900, 45.

Volume, specific, of diisopropyl and diisobutyl (YOUNG and FORTEY), T., 1126; P., 1900, 165.

of *n*-octane (YOUNG), T., 1145; P., 1900, 166.

## W.

Water, conductivity of, distilled in air (WALKER and CORMACK), T., 11.

Willow bark, new glucoside from (JOWETT), T., 707; P., 1900, 89.

Xylenes, *o*-, *m*-, and *p*-, refraction and magnetic rotation of (PERKIN), T., 267; P., 1899, 237.

Xylidines, isomeric, separation of, from commercial xylidine (HODGKINSON and LIMPACH), T., 65; P., 1899, 202.

## Z.

Zinc alloys with copper, heat of combination of (BAKER), P., 1899, 185.

Zinc sulphate, combination of, with ammonia in aqueous solution (DAWSON and McCRAE), T., 1245; P., 1900, 173.

hydroximidosulphate, production of (DIVERS and HAGA), T., 690; P., 1900, 71.

potassium sulphate (MALLET), T., 220; P., 1899, 227.





# ERRATA.

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Page	Line	
82	bottom	for "maleic" read "malic."
139	8*	„ "mixture of iodate (the iodine) and iodide of potassium to be titrated" read "mixture of iodate and iodide of potassium (the iodine to be titrated)."
437	22	„ "1870" read "1871."
444	9*	} „ "nitrito" read "nitrogen."
446	1	
499	10	„ "active" read "inactive."
„	22, 23	delete "with right- and left-handed rotation."
936	24	should read "0.2415 gave 0.1268 Na <sub>2</sub> SO <sub>4</sub> . Na=17.01.
„	4*	„ "0.2357 gave 0.1551 Na <sub>2</sub> SO <sub>4</sub> . Na=21.34.
„	3*	„ C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> NNa requires Na=21.49 per cent."
982	20	} for "litmus" read "lacmoid paper."
983	11	
982	5	after "then" insert " , after neutralisation."
1053	16	for "units" read "union."
1206	10*	„ "1-chloro-1 : 2-phenylenediamine" read "1-chloro-2 : 4-phenylenediamine."
1213	20	„ "loc. cit." read "Annalen, 1898, 302, 313."
1218	15	„ "C <sub>19</sub> H <sub>15</sub> ONCl" read "C <sub>19</sub> H <sub>15</sub> ON <sub>2</sub> Cl."
1264	6*	$\begin{array}{c} \text{H}_2\text{C}\cdot\text{NH} \\   \\ \text{O} \\    \\ \text{HO}\cdot\text{N}:\text{C}\cdot\text{O} \end{array} \quad \text{read} \quad \begin{array}{c} \text{H}_2\text{C}\cdot\text{NH} \\   \\ \text{O} \\    \\ \text{HO}\cdot\text{N}:(\text{O}) \end{array}$

\* From bottom.

I. A. B. I. 75.

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